

DATE LABEL

07.-8.97			
08			
23/7			

Call No.....539-72 N462B

Date.3.3.56.....

Account No.....14251

J. & K. UNIVERSITY LIBRARY

This book should be returned on or before the last stamped above.
An overdue charges of 6 nP. will be levied for each day ~~8~~ 7 the book is kept beyond that day.

619

Title

Author

Accession No.

Call No.

Borrower's
No.

Issue
Date

Borrower's
No.

Issue
Date

Title

Author

Accession No.

Call No.

Borrower's
No.

Issue
Date

Borrower's
No.

Issue
Date

ELECTROLYTIC CONDUCTION

Title

Author

Accession No.

Call No.

Borrower's
No.

Issue
Date

Borrower's
No.

Issue
Date

ELECTROLYTIC CONDUCTION

BY

F. H. NEWMAN,

D.Sc., A.R.C.S., F.INST.P.

PROFESSOR OF PHYSICS, UNIVERSITY COLLEGE OF THE SOUTH-WEST
OF ENGLAND, EXETER

1830



1930

CHAPMAN & HALL'S
CENTENARY YEAR

333

CHECKED

DM

ALLAMA IQBAL LIBRARY
14251

LIBRARY
No. 14.251.
Date 3.3.56

8682

101
TNB

539.12
N 462 E.

PREFACE.

THIS book is an attempt to give the reader some idea of the fundamental conceptions underlying the ionic theory, more particularly as applied to the passage of electricity through electrolytes, a subject which has attracted the attention of physicists and physical chemists for many years, and in which there is a vast accumulation of important data, not always of that degree of accuracy necessary to guide hypotheses and co-ordinate theories. However, during the past six years Debye and Hückel have formulated a theory which, under certain conditions, satisfactorily accounts for the electrical conductance of strong electrolytes, and the success which attended their efforts has stimulated other workers to make a more detailed study of the subject. We still remain without a clear conception of why an electrolyte, in the first instance, should dissociate, and an explanation is not likely to be forthcoming until many more very accurate measurements have been made of the properties of electrolytes, both in aqueous and non-aqueous solvents.

Unfortunately the information and experimental data relating to electrolytic conduction lie widely scattered through volumes of the various scientific and technical journals. These known facts have been collected, and in the present book they are presented, together with the theoretical views which serve to connect them, in an ordered sequence. It is not an easy matter to arrange a mass of branching and inter-related ideas in serial order, and the author cannot hope that the particular sequence, which seems to him the best, will necessarily appeal to all readers.

Since the use of modern thermodynamic methods is extending to almost all branches of the subject, and since such methods may be unfamiliar to some students, an introductory chapter has

been introduced, explaining all of the thermodynamic principles which are applied in the work. The succeeding chapters are chiefly devoted to the properties of electrolytic solutions, aqueous and non-aqueous, and a fairly full account of the modern theories of electrolytic conduction has been given, especially that of Debye and Hückel, which has not heretofore appeared in English. In addition to the theoretical views and the known facts, the more important experimental methods, used in determining these facts, have been fully described. The last chapter contains a brief account of the technical applications of electrolysis.

The necessary mathematics are simple, but it has been assumed that students, who use the book, will be sufficiently familiar with the fundamental processes of the calculus to follow its methods, and appreciate its advantages.

Throughout the treatise numerous references are given in footnotes to scientific and technical literature, and these should be consulted by the reader who wishes to obtain more detailed information concerning any given part of the subject. As the literature has been freely utilised, it is hoped that adequate credit has been accorded at the appropriate places in the text. A bibliography is given at the end of each chapter, and since all such bibliographies must necessarily be incomplete, the main principle in the compilation has been to include a full representative selection of the research in each branch of the work.

Finally, to minimise time and annoyance, a list of symbols, used throughout the book, has been included.

F. H. N.

EXETER,

September, 1930.

CONTENTS.

	PAGE
PREFACE	V
NOTATION	xi

CHAPTER I.

THERMODYNAMIC PRINCIPLES		I
1. The first law of thermodynamics. 2. The second law of thermodynamics. 3. Entropy. 4. Thermodynamic potential and free energy. 5. The Nernst heat theorem. 6. Clapeyron's equation. 7. The equilibrium of systems. 8. The phase rule. 9. Osmotic pressure. 10. Vapour pressure of a solution. 11. Boiling-point temperature of a solution. 12. Freezing- point temperature of a solution. 13. Molecular weights. 14. The law of mass action. 15. Variation of the equilibrium constant with temperature. 16. Gibbs's adsorption equation. Bibliography.		

CHAPTER II.

ELECTROLYSIS		25
17. Introduction. 18. Electrolysis. 19. Faraday's law of electrolysis. 20. Voltameters. 21. Theoretical considerations. 22. Electro-chemical equivalents. Bibliography.		

CHAPTER III.

ELECTROLYTIC CONDUCTANCE OF SOLUTIONS		36
23. The electrolytic conduction process. 24. Equivalent conductivity. 25. Determination of the degree of ionisation. 26. Independent migration of the ions. 27. Conductance, or mobility, of the ions. 28. Ionic mobility and temperature. 29. Law of mass action applied to electrolytes. 30. Strong electrolytes. 31. Conductivity of non-aqueous solutions. 32. Conductivity of salts in alcohols. 33. Conductivity of liquid ammonia solutions at -33°C . 34. Conductivity of liquid sulphur dioxide solutions. 35. Conductivity of liquid hydrogen bromide solutions. 36. Conductivity of salt solutions in other solvents. 37. Mass action law for non-aqueous solutions. 38. Conductivity of alkali metals in liquid ammonia. 39. Conductivity of salts in mixed solvents. 40. Conductivity of soap solutions. 41. Conductivity of fused electrolytes. 42. Conductivity and concentration. 43. The relation between conductivity and viscosity. 44. Conductivity and temperature. Bibliography.		

CHAPTER IV.

	PAGE
THE MIGRATION OF THE IONS	97
45. Material effects accompanying the conduction process. 46. Concentration changes produced by current. 47. Experimental determination of transference numbers. 48. Change of transference number with concentration and temperature. 49. Solvation of the ions. 50. True transference numbers. 51. True mobilities. 52. Moving boundary method of determining transference numbers. 53. Transference numbers in non-aqueous solvents. 54. Transference numbers in mixed solutions. 55. Importance of transference numbers. 56. Absolute velocity of the ions. 57. Dimensions of ions. 58. Complex ions. Bibliography.	

CHAPTER V.

HOMOGENEOUS IONIC EQUILIBRIA	132
59. Equilibria of mixed electrolytes. 60. The conductivity of mixed electrolytes. 61. Dissociation of water. 62. Solubility of electrolytes. 63. Solubility in non-aqueous solvents. 64. Osmotic phenomena. 65. Freezing-point temperature depression. 66. Boiling-point temperature elevation. 67. Thermal properties of electrolytes. 68. The heat of dissociation of water. 69. The heat of neutralisation. 70. Optical properties of electrolytic solutions. 71. Other additive properties of electrolytes. 72. Diffusion. 73. Diffusion in electrolytic solutions. Bibliography.	

CHAPTER VI.

CELLS AND ELECTROMOTIVE FORCE	174
74. Introduction. 75. Reversible and non-reversible cells. 76. Calculation of the electromotive force of a reversible voltaic cell. 77. Calculation of the potential difference at a metal-solution interface. 78. Theories of the electrode potential. 79. Variation of the electromotive force of a cell with concentration. 80. Standard electrodes. 81. The normal hydrogen electrode. 82. Working standard half-cells. 83. The quinhydrone electrode. 84. Dropping electrodes. 85. Normal electrode potentials. 86. Concentration cells. 87. Thermodynamics of concentration cells. 88. Concentration cells with transference. 89. Concentration cells without transference. 90. Measurement of the electromotive force of a concentration cell. 91. Liquid-liquid potentials. 92. Flowing junctions. 93. Diffusion potentials. 94. Standard cells. 95. Transference numbers from electromotive force measurements. 96. Concentration cells containing mixed electrolytes. 97. Amalgam concentration cells. 98. Concentration cells with non-aqueous solutions. 99. Temperature coefficient of concentration cell. 100. Gas cells. 101. Oxidation-reduction cells. 102. Oxidation potential. 103. Measurement of oxidation potential. 104. Applications of concentration cells. 105. Irreversible cells. 106. Photo-voltaic cells. 107. Individual ionic heat contents. Bibliography.	

CHAPTER VII.

ELECTRO-CAPILLARITY	257
108. Electro-capillary effects. 109. Theoretical considerations. 110. Electro-capillary phenomena at other interfaces. 111. Theories of electro-capillarity. 112. The absolute zero of potential. 113. Electro-kinetic phenomena. Bibliography.	

CHAPTER VIII.

	PAGE
POLARISATION	276
114. Polarisation. 115. Back electromotive force. 116. Decomposition voltage. 117. Overvoltage. 118. Measurement of overvoltage. 119. Comparison of the methods of measuring overvoltage. 120. Kathodic overvoltage. 121. Anodic overvoltage. 122. Experimental results. 123. The variation of overvoltage. 124. Transfer resistance. 125. Theories of hydrogen overvoltage. 126. Theories of oxygen overvoltage. 127. Passivity. 128. Alternating current electrolysis. 129. Accumulators. Bibliography.	

CHAPTER IX.

THE MEASUREMENT OF ELECTROLYTIC RESISTANCE	311
130. Introduction. 131. Experimental determination of electrolytic resistance. 132. Errors in the Kohlrausch bridge method. 133. Experimental results. 134. Conductivity cells. 135. Conductivity water. 136. Correction for the conductivity of water. 137. Conductivity of very weak solutions. 138. Polarisation capacity. 139. Resistance of fused electrolytes. Bibliography.	

CHAPTER X.

THEORIES OF ELECTROLYTIC SOLUTION	339
140. Preliminary considerations. 141. Ostwald's dilution law. 142. Anomaly of strong electrolytes. 143. Complete dissociation. 144. Ghosh's theory. 145. Milner's theory. 146. Debye and Hückel's theory. 147. Onsager's theory. 148. The dielectric constant of electrolytic solutions. 149. The Wien effect. 150. Conductance dispersion. 151. Activity theory. Bibliography.	

CHAPTER XI.

TECHNICAL APPLICATIONS OF ELECTROLYSIS	379
152. Electrolytic deposition. 153. Current efficiency. 154. Alloys. 155. The electrolysis bath. 156. Electro-plating. 157. Electrolytic extraction and refining of metals. 158. Fused electrolytes. 159. The anode effect. 160. The electrolysis of brine. 161. Technical cells. 162. Other electrolytic processes. Bibliography.	

APPENDIX I.

POISSON'S EQUATION	413
------------------------------	-----

APPENDIX II.

THE MOTION OF AN ION IN A SOLUTION	415
NAME INDEX	427
SUBJECT INDEX	434

Title

Author

Accession No.

Call No.

[illegible]

NOTATION.

- | | |
|--|--|
| <p><i>a.</i> Activity.</p> <p><i>b.</i> Radius of ion.</p> <p><i>c.</i> Electrostatic capacity.</p> <p><i>e.</i> Electrical charge on ion.</p> <p>e_0. Unit of electrical charge.</p> <p><i>f.</i> Fugacity; fluidity.</p> <p><i>i.</i> Electric current; van't Hoff factor.</p> <p><i>k.</i> Boltzmann's constant; various other constants.</p> <p>k_m. Molecular refraction.</p> <p><i>m.</i> Mass.</p> <p><i>n.</i> Number of ions per molecule; number of moles of solute.</p> <p>n_A. "Hittorf" transference number of anion; gram anions per mole.</p> <p>n_K. "Hittorf" transference number of kation; gram kations per mole.</p> <p><i>p.</i> Hydrostatic pressure; vapour pressure; solution pressure.</p> <p>q_{Hg}^+. Electrical charge on mercury ion.</p> <p><i>s.</i> Solubility.</p> <p>s_0. Solubility product.</p> <p><i>t.</i> Time; degrees Centigrade.</p> <p>u_A. Velocity of anion under unit potential gradient.</p> <p>u_K. Velocity of kation under unit potential gradient.</p> <p>u_A°. Velocity of anion at infinite dilution.</p> <p>u_K°. Velocity of kation at infinite dilution.</p> <p><i>v.</i> Volume of gas; volume of solvent.</p> <p><i>x.</i> Generalised co-ordinate.</p> <p><i>z.</i> Electro-chemical equivalent.</p> <p><i>A.</i> Area.</p> <p><i>C.</i> Concentration of solution.</p> <p><i>D.</i> Specific inductive capacity.</p> <p><i>E.</i> Internal energy.</p> | <p>\bar{E}. Virial of forces.</p> <p><i>F.</i> The faraday—96,491 coulombs.</p> <p><i>H.</i> Total heat contents.</p> <p>H_p, H_v. Heats of dissociation at constant pressure and volume, respectively.</p> <p><i>K.</i> Equilibrium constant.</p> <p><i>L.</i> Latent heat.</p> <p><i>M.</i> Molecular weight.</p> <p><i>N.</i> Number of molecules per mole; moles per c.c. of solution.</p> <p><i>P.</i> Osmotic pressure; polarisation.</p> <p><i>Q.</i> Quantity of heat; quantity of electricity.</p> <p><i>R.</i> Gas constant per mole; electrolytic resistance.</p> <p><i>S.</i> Surface tension.</p> <p><i>T.</i> Temperature (absolute).</p> <p><i>U.</i> Mobility or conductance of kation.</p> <p><i>V.</i> Mobility or conductance of anion.</p> <p>U_0, V_0. Mobilities at infinite dilution.</p> <p><i>W.</i> Work.</p> <p><i>X.</i> Generalised force.</p> <p><i>C.</i> Centigrade scale.</p> <p><i>N.</i> Normal, a concentration of one gram-equivalent per litre.</p> <p>[C]. Concentration of ions.</p> <p>[M⁺]. Concentration of M⁺ ions.</p> <p>[MX]. Concentration of salt, MX.</p> <p><i>M.</i> Molality. The number of moles of a solute in 1000 grams of solvent.</p> <p><i>m.</i> Molarity. The number of moles of a solute in 1 litre of solution.</p> <p>n_A. True transference number of anion.</p> <p>n_K. True transference number of kation.</p> <p>u_A. Observed velocity of anion.</p> <p>u_K. Observed velocity of kation.</p> |
|--|--|

D. Diffusion coefficient.	ζ . Friction coefficient.
E. Electromotive force of cell.	τ . Molecular depression of freezing-point temperature.
E_p. Back electromotive force.	μ . Refractive index; ionic strength.
F. Thermodynamic potential at constant pressure. Free energy at constant pressure.	π . Electrode potential.
N_W. Number of water molecules carried by ion.	ϕ . Entropy.
P. Property of substance.	σ . Density of vapour; electrical specific conductivity.
Q₀. Charge in coulombs per sq. cm. of double layer at interface.	ρ . Density of solution; density of ion.
U, V. True ionic mobilities of kation and anion, respectively.	ν . Valency of ion.
α . Fraction of molecules ionised.	κ . Specific resistance; constant in Debye and Hückel's theory.
γ . Activity coefficient.	Λ . Equivalent conductance.
ψ . Electrical potential; free energy at constant volume.	η . Coefficient of viscosity.
	e . The electron.
	\log . Napierian logarithms.
	\log_{10} . Common logarithms.

CHAPTER I.

THERMODYNAMIC PRINCIPLES.

1. The first law of thermodynamics.—Thermodynamics is that branch of science which deals with the relationships governing the quantitative transformations of energy from one form to another. There are many applications of thermodynamics to physical and chemical problems, and for this reason it is proposed to consider in this first chapter some of the more important thermodynamic principles.

There are two main laws of thermodynamics known as the *first* and *second* laws, respectively, but another principle has been put forward by Nernst * and is often referred to as a *third* law.

Any system in a given state possesses energy which is associated with the nature, configuration and motion of its constituents. If the system passes from one state to another, the resulting change in this *internal energy* is independent of the manner in which the change is made, and depends only upon the nature, disposition and motion, if any, of the constituents in the respective states. Absorption, or evolution, of heat, and work of any type done by, or on, the system, affect its internal energy content, the amount of the heat change depending upon the type of process which occurs. If δE is the very small change in the internal energy which accompanies the absorption † of a very small quantity, δQ , of heat, both measured in *work units*, and δW is the very small amount of work, of any type, done by the system at the same time, then,

$$\delta E = \delta Q - \delta W. \quad . \quad . \quad . \quad (1)$$

For example, if the work done is entirely expended against a uniform hydrostatic pressure, p , then $\delta W = p\delta v$, and

$$\delta E = \delta Q - p\delta v,$$

where δv is the resulting volume change. If the system consists of a perfect gas, and it expands *isothermally*, the original and final

* *The New Heat Theorem*, 1926.

† Heat absorbed by a system is denoted by the *positive* sign, and that evolved by the *negative* sign. In a similar manner work done *on* and *by* a system is denoted by the *positive* and *negative* signs, respectively.

volumes being v_1 and v_2 , respectively, the total work done by the gas is

$$\int_{v_1}^{v_2} p \delta v, \text{ i.e., } RT \log \frac{v_2}{v_1}, \text{ or } RT \log \frac{p_1}{p_2},$$

where T is the temperature measured on the gas scale, and R the gas constant, p_1 and p_2 being the initial and final pressures, respectively.

2. The second law of thermodynamics.—A substance, or system, may be subjected to a complete cycle of operations and return to its original state. In this case the net change of internal energy is zero, the net heat absorbed being equal to the total work performed by the substance. A process may be carried out under *isothermal* conditions, i.e., constant temperature, or under *adiabatic* conditions when there is neither liberation nor absorption of heat. As a rule, both types of processes occur during a complete cycle of operations.

A process is said to be *reversible* in the thermodynamic sense if it is possible for the successive stages to occur in exactly the reverse order with all the mechanical forces unaltered. Thus, if the expansion of a gas is carried out sufficiently slowly for the substance to be in equilibrium with the external pressure at any stage, the process is reversible; but it must be borne in mind that a reversible process or cycle is one that can never be realised in practice.

Consider an ideal cycle such as that proposed by Carnot. A substance expands under isothermal conditions, and in doing so, it absorbs a quantity of heat Q_1 at an absolute temperature T_1 . It is then allowed to expand adiabatically until its temperature falls to T_2 . Compressing it isothermally, heat equal to Q_2 is abstracted, the temperature remaining at T_2 ; and finally the substance is brought back to its original state by means of a suitable adiabatic compression. Such a cycle is perfectly reversible, and $Q_1 - Q_2 = W$ is the mechanical work done during the cycle. The efficiency of the cycle is the ratio of the mechanical work performed to the heat absorbed, i.e., $\frac{Q_1 - Q_2}{Q_1}$, and it may be proved that the efficiency is equal to $\frac{T_1 - T_2}{T_1}$, so that

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}, \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

where the temperatures are measured on the absolute work scale.*

* A temperature measured on the work scale is practically equal in value to that on the gas scale.

Thus, the maximum amount of work derivable from a given quantity of heat, supplied to a substance, is obtained when Q_2 is zero, and it is evident that any self-acting machine, performing the above cycle, cannot convey heat from one body to another at a higher temperature unless that machine is aided by external agency. This axiom is known as the *second law of thermodynamics*. It will be noted that in any reversible process, where heat is developed from mechanical energy, there is no waste or dissipation of energy.

The Carnot cycle is one of the simplest reversible processes to which a system may be subjected ; and usually the cycle followed in practice is more complex. We may, however, write equation (2) in the form,

$$\sum \frac{Q}{T} = 0,$$

and in general for any reversible cycle, if δQ is the very small amount of heat taken in at a temperature T ,

$$\sum \frac{\delta Q}{T} = 0.$$

This result is known as the *Carnot-Clausius* equation.

For an *irreversible cycle*,

$$\sum \frac{\delta Q}{T} < 0,$$

the irreversible processes which may occur in the cycle including the production of heat by friction, conduction and radiation of heat and change of internal energy brought about by expansion.

3. Entropy.—If a substance absorbs a small quantity, δQ , of heat isothermally at a temperature T , the ratio $\frac{\delta Q}{T}$ represents what is known as the increase in the *entropy* of the substance. Denoting this ratio by $\delta\phi$, we have

$$\delta Q = T\delta\phi,$$

and we see from equation (2) that in a Carnot cycle the net change of entropy is zero. In fact, for any perfectly reversible cycle the total change in the entropy of the substance subjected to the cycle is zero. This result may be stated in another way. If a substance passes from one state to another by a reversible process, the increase of entropy is independent of the process or path taken, and depends only upon the initial and final states.

In natural processes, which are practically irreversible in all cases, the entropy of a system increases. For example, heat is always conducted from places of higher, to those of lower, temperatures, so that if δQ is the amount of heat which passes from a body at a temperature T_1 to one whose temperature is T_2 , then $\frac{\delta Q}{T_2} - \frac{\delta Q}{T_1}$ is the net gain in entropy. Since $T_2 < T_1$ the total entropy of the two bodies is raised by the conduction process.

4. Thermodynamic potential and free energy.—The mechanical work done on, or by, a system may be expressed as the product of a pressure and a volume, but there are other pairs of quantities such as, for example, electromotive force and quantity of electricity, which, when multiplied together, give quantities having the dimensions of energy. In general, the work done by a system is not entirely of a mechanical nature, but may consist of various forms of energy. Whatever the form may be, each type of energy may be expressed as a product of two terms, one of which is a *co-ordinate* defining some *quantity*, such as volume, quantity of electricity, *etc.*, in the system, the other term being an *intensity factor* such as pressure or electromotive force. Since all forms of energy are mutually convertible, they have the same dimensions, and for this reason we may group all the energy expended, or work done, by, or on, a system in a single term of the form,

$$\Sigma(X\delta x),$$

where factors similar to X are the intensity factors, or *generalised forces*, and factors of the form x are the quantity factors, or *generalised co-ordinates*. Hence, the first law of thermodynamics, equation (1), may be written in the general form,

$$\delta E = \delta Q - \Sigma(X\delta x).$$

Since $\delta Q = T\delta\phi$ we have

$$\delta E = T\delta\phi - \Sigma(X\delta x),$$

which may be written in the form,

$$\delta(E - T\phi) = -\phi\delta T - \Sigma(X\delta x). \quad . \quad . \quad (3)$$

If we write ψ for $E - T\phi$ then,

$$\delta\psi = -\phi\delta T - \Sigma(X\delta x), \quad . \quad . \quad . \quad (4)$$

which, it should be noted, is only true for a reversible transformation. When the conditions are isothermal,

$$\delta\psi = -\Sigma(X\delta x),$$

— $\Sigma(X\delta x)$ denoting the external work which can be obtained from the system during an infinitesimal isothermal variation. Denoting by W the work which the system can give in passing, isothermally, from the state A to the state B,

$$\psi_B - \psi_A = \int_A^B \Sigma(X\delta x) = -W,$$

and thus, $W = \psi_A - \psi_B$.

The function ψ is known as the *thermodynamic potential at constant volume*, and we see that the work obtainable from the system, during an isothermal process, is equal to the decrease in its thermodynamic potential for a reversible process. Thus, the decrease in the function ψ represents the *maximum amount of available, or free, energy* which can be extracted from a system during isothermal processes, and for this reason Helmholtz called ψ the free energy of the system.

From equation (4) we have, when x , etc., is constant,

$$\phi = -\frac{\partial \psi}{\partial T},$$

and since

$$\psi = E - T\phi,$$

$$\psi = E + T\left(\frac{\partial \psi}{\partial T}\right)_v. \quad . \quad . \quad . \quad (5)$$

This result is known as the *Gibbs-Helmholtz equation*,* and since the equation is linear, E and ψ may represent differences of the internal and free energies of two given states. As a rule it is so used. It gives the free energy, or maximum work, which the system is capable of providing, but the complete utilisation of this free energy is only conceivable in the case of reversible changes. In reality any process can occur only more or less approximately in a reversible manner; part of the free energy is always lost in overcoming unavoidable frictional resistances.

Now equation (3) may be written in the form,

$$\delta[E - T\phi + \Sigma(Xx)] = -\phi\delta T + \Sigma(x\delta X),$$

and if we write \mathbf{F} for $[E - T\phi + \Sigma(Xx)]$,

$$\delta\mathbf{F} = -\phi\delta T + \Sigma(x\delta X). \quad . \quad . \quad . \quad (6)$$

Although the external generalised forces may be constant, this fact does not exclude external work equal to $\Sigma(X\delta x)$ from being

* See Thomson, *Collected Papers*, vol. 1, p. 297.

done, and for this reason \mathbf{F} has been called the *total thermodynamic potential*. If the only external generalised force is a uniform pressure, p , and the only external co-ordinate the volume, v , then,

$$\delta \mathbf{F} = -\phi \delta T + v \delta p. \quad . \quad . \quad . \quad (7)$$

In isothermal systems equilibrium is reached, at constant pressure, when \mathbf{F} is a minimum, and on this account \mathbf{F} is called the *thermodynamic potential at constant pressure*.

From equation (6) we have, when X, \dots is constant,

$$\phi = -\frac{\partial \mathbf{F}}{\partial T},$$

and since $\mathbf{F} = [E - T\phi + \Sigma(Xx)]$, we have

$$\mathbf{F} = H + T\left(\frac{\partial \mathbf{F}}{\partial T}\right)_p, \quad . \quad . \quad . \quad (8)$$

where $H = E + \Sigma(Xx)$, and may be called the *total heat content* of the system. Lewis* and American writers define the free energy of a system by the function \mathbf{F} , since most experiments are carried out under constant pressure conditions. Although changes in the functions ψ and \mathbf{F} do not largely differ, numerically, it is unfortunate that the term free energy is applied to two different quantities, but, if it is remembered that the function $\delta\psi$ refers to changes in the free energy at constant volume, and $\delta\mathbf{F}$ to changes in the free energy at constant pressure, confusion between these two quantities is not likely to arise.

5. The Nernst heat theorem.—Since equation (5) may be written in the form,

$$\frac{d}{dT}\left(\frac{\psi}{T}\right) = -\frac{E}{T^2},$$

we have, on integrating,

$$\psi = -T \int \frac{E}{T^2} dT, \quad . \quad . \quad . \quad (9)$$

but the value of this integral cannot be obtained unless E is known as a function of T . Nernst† assumed that

$$E = E_0 + \alpha T + \beta T^2 + \gamma T^3 + \rho T^4 + \dots, \quad . \quad . \quad . \quad (10)$$

where α, β, \dots are known from experimental determinations of the specific heats at constant volume of the system before and

* See Lewis and Randall, *Thermodynamics* (1923).

† *Nachr. kgl. Ges. Wiss. Göttingen. Math.-physik. Klasse*, 1 (1906).

after chemical, or physical, changes.* Therefore,

$$\psi - T \frac{d\psi}{dT} = E_0 + \alpha T + \beta T^2 + \gamma T^3 + \rho T^4 + \dots,$$

or

$$- T^2 \frac{d}{dT} \left(\frac{\psi}{T} \right) = E_0 + \alpha T + \beta T^2 + \gamma T^3 + \rho T^4 + \dots$$

Integrating, we have,

$$\psi = E_0 + AT - \alpha T \log T - \beta T^2 - \frac{\gamma T^3}{2} - \frac{\rho T^4}{3} - \dots,$$

where A is a constant of integration. Hence,

$$\frac{d\psi}{dT} = A - \alpha(1 + \log T) - 2\beta T - \frac{3}{2}\gamma T^2 - \frac{4}{3}\rho T^3 - \dots,$$

and from equation (10),

$$\frac{dE}{dT} = \alpha + 2\beta T + 3\gamma T^2 + 4\rho T^3 + \dots$$

From these various results we see that as T approaches zero ψ tends to the value E_0 , E to E_0 and $\frac{dE}{dT}$ to α , whereas $\frac{d\psi}{dT}$ tends to infinity. We should expect ψ , like E , to show a simple behaviour at low temperatures, and not to produce the anomaly of $\frac{d\psi}{dT}$ approaching the value infinity. This anomaly is removed if $\alpha = 0$, in which case

$$\frac{dE}{dT} = 2\beta T + 3\gamma T^2 + 4\rho T^3 + \dots$$

and
$$\frac{d\psi}{dT} = A - 2\beta T - \frac{3}{2}\gamma T^2 - \frac{4}{3}\rho T^3 - \dots,$$

Nernst suggested that $\frac{dE}{dT} = \frac{d\psi}{dT} = 0$ at the absolute zero, $T = 0$, and therefore $A = 0$. Thus,

$$\frac{dE}{dT} = 2\beta T + 3\gamma T^2 + 4\rho T^3 + \dots,$$

$$\frac{d\psi}{dT} = -2\beta T - \frac{3}{2}\gamma T^2 - \frac{4}{3}\rho T^3 - \dots,$$

* See Kirchhoff, *Ann. d. Phys.*, 103, 177 (1858).

$$\left. \begin{array}{l} \text{and} \quad E = E_0 + \beta T^2 + \gamma T^3 + \rho T^4 + \dots, \\ \text{also,} \quad \psi = E_0 - \beta T^2 - \frac{1}{2}\gamma T^3 - \frac{1}{3}\rho T^4 - \dots \end{array} \right\} \quad (11)$$

These formulæ cannot hold down to very low temperatures, since Debye's* theory requires the specific heat at low temperatures to vary as T^3 , i.e., $\frac{dE}{dT}$ must be proportional to T^3 . Thus $\beta = \gamma = 0$ and

$$\begin{aligned} E &= E_0 + \rho T^4 + \dots, \\ \psi &= E_0 - \frac{1}{3}\rho T^4 - \dots \end{aligned}$$

6. Clapeyron's equation.—If the only external co-ordinate is the volume, v , and the only external generalised force which the system exerts is a uniform pressure, p , then equation (4) may be written thus :—

$$\delta\psi = -\phi\delta T - p\delta v,$$

so that

$$\left(\frac{\partial\psi}{\partial v}\right)_T = -p,$$

and

$$\left(\frac{\partial\psi}{\partial T}\right)_v = -\phi.$$

Thus,

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial\phi}{\partial v}\right)_T.$$

Hence for a substance present in two states, these states being in equilibrium, such as, for example, a liquid in contact with its vapour, if v_2 and v_1 are the specific volumes of the substance in the two states, respectively, L the latent heat of change of state, then,

$$\delta\phi = \frac{L}{T},$$

and

$$\frac{\partial p}{\partial T} = \frac{L}{T(v_2 - v_1)}.$$

This result is known as *Clapeyron's equation*, and it is of great importance in the study of many physical and chemical changes. Thus, it represents the effect of pressure both on the boiling-point temperature of a solution and on the melting-point temperature

* *Ann. d. Phys.*, 39, 789 (1912).

of solids, δT being the change in these temperatures produced by a change in pressure equal to δp . If $v_2 > v_1$, then $\frac{\delta T}{\delta p}$ is positive, *i.e.*, the boiling-point temperature of a liquid is raised with pressure, whereas the freezing-point temperature of water, for which $v_2 < v_1$, is lowered by pressure.

7. The equilibrium of systems.—In any natural change it is evident that the temperature of the substance must be less than that of the source which supplies heat to it, or greater than that of the surroundings to which it ejects heat. In other words, instead of the relation given by equation (2) we have

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1},$$

or, more generally,

$$\sum \frac{\delta Q}{T} < 0.$$

The interpretation of this is, that if a system passes from a state A to another state B by means of a reversible process, absorbing heat δQ at a constant temperature, and then returns to its original state by an irreversible process, losing entropy $\delta \phi$,

$$\frac{\delta Q}{T} - \delta \phi < 0,$$

or

$$\delta Q < T \delta \phi,$$

i.e., putting

$$\delta Q = \delta E + p \delta v,$$

$$\delta E < T \delta \phi - p \delta v,$$

and

$$\delta(E - T \phi) < -\phi \delta T - p \delta v.$$

Also,

$$\delta(E - T \phi + p v) < -\phi \delta T + v \delta p.$$

Hence, if the volume of a system remains constant during an irreversible isothermal change,

$$\delta(E - T \phi), \text{ i.e., } \delta \psi < 0,$$

and if the pressure and temperature remain constant,

$$\delta(E - T \phi + p v), \text{ i.e., } \delta \mathbf{F} < 0.$$

We conclude, therefore, that if,

(a) v and T remain constant in any non-isolated system, the function ψ cannot increase.

(b) p and T remain constant in any non-isolated system, the function \mathbf{F} cannot increase.

From (a) we infer that when ψ is a minimum, no change can take place, and consequently the system under the conditions defined by (a) is in stable equilibrium. Also from (b) we infer that the system will be in equilibrium when \mathbf{F} is a minimum.

If the system is not homogeneous throughout, but consists of masses $m_1, m_2, \text{etc.}$, of different qualities, or in different states, the internal energy, E , of the whole is given by the sum of the internal energies of the constituents. Thus, if $E_1, E_2, \text{etc.}$, be the internal energies, per unit mass of the constituents,

$$E = m_1 E_1 + m_2 E_2 + \dots$$

Similarly, if $\phi_1, \phi_2, \text{etc.}$, be the entropies per unit mass of the different constituents, then,

$$\phi = m_1 \phi_1 + m_2 \phi_2 + \dots$$

Now, at constant temperature and pressure E is a function of ϕ, v and m , the total mass present in the mixture, so that

$$\delta E = \frac{\partial E}{\partial \phi} \delta \phi + \frac{\partial E}{\partial v} \delta v + \frac{\partial E}{\partial m_1} \delta m_1 + \dots \quad (12)$$

and if the total mass remains constant,

$$\delta E = T \delta \phi - \Sigma (X \delta x),$$

or, in the case of a hydrostatic pressure, p ,

$$\delta E = T \delta \phi - p \delta v,$$

i.e.,

$$\left(\frac{\partial E}{\partial \phi} \right)_v = T; \left(\frac{\partial E}{\partial v} \right)_\phi = -p. \quad (13)$$

Hence from equations (12) and (13),

$$\delta E = T \delta \phi - p \delta v + \frac{\partial E}{\partial m_1} \delta m_1 + \dots \quad (14)$$

and, therefore, by summation,

$$E = T \phi - p v + \sum \frac{\partial E}{\partial m_1} \delta m_1 \dots \quad (15)$$

Thus, remembering that $E - T \phi = \psi$, and $E - T \phi + p v = \mathbf{F}$, we obtain,

$$\psi = -p v + \sum \frac{\partial E}{\partial m_1} \delta m_1 \dots \quad (16)$$

and

$$\mathbf{F} = \sum \frac{\partial E}{\partial m_1} \delta m_1 = \mathbf{F}_1 m_1 + \dots,$$

where $\mathbf{F}_1 = \frac{\partial E}{\partial m_1}$, and is the increase of internal energy of the mixture per unit mass addition of the first constituent, the temperature and pressure remaining constant.

Consider a system of unit mass of any substance existing in two states, say liquid and vapour, and let a mass δm of liquid change into vapour. Then at constant temperature and pressure,

$$\delta \mathbf{F} = \mathbf{F}_1 \delta m - \mathbf{F}_2 \delta m. \quad (17)$$

In equilibrium \mathbf{F} is a minimum and so $\delta \mathbf{F} = 0$, thus,

$$\mathbf{F}_1 = \mathbf{F}_2,$$

and the potentials of the substance are the same in each phase. This result is true, however many phases of the one substance are present, so that in general,

$$\mathbf{F}_1 = \mathbf{F}_2 = \mathbf{F}_3 = \dots$$

8. The Phase Rule.—If a system contains n components and r phases, it is evident from equation (17) that we may obtain $(r - 1)$ independent equations for each component, or $n(r - 1)$ equations in all. Within unit mass of each phase there may be n components, and if the masses of $(n - 1)$ of these are known, the composition of the phase is determinable. Since there are r phases of each component, $r(n - 1)$ is the number of independent variables defining the whole system. The temperature and pressure are also independent variables, but the volume is then fixed. Thus the total number of variables attaching to the system is $r(n - 1) + 2$, and there are $n(r - 1)$ equations to determine them. If

$$r(n - 1) + 2 = n(r - 1),$$

the variable can have only one determinate value, and the system is in equilibrium at one pressure, one temperature, and a fixed composition of the variable phase. For example, consider one component in three phases—ice, water and water vapour—in contact. Here $n = 1$ and $r = 3$, so that if we fix the temperature and pressure the system is *non-variant*. The three phases can only exist in contact at a definite temperature and pressure—the *triple point*.

On the other hand, if the number of variables exceeds the number of independent equations, the system will not be completely determined; different equilibrium conditions will be possible. Thus there are

$$r(n - 1) + 2 - n(r - 1)$$

variables which are arbitrary, and the number— $(n - r + 2)$ —of independent variables is called the number of *degrees of freedom*. This relation, which is known as the *phase rule*, may be stated as follows. *For a system in equilibrium, the number of degrees of freedom is two more than the excess number of components over the number of co-existing phases.*

With a solution of salt in water, if we suppose the salt is non-volatile and that there is excess of water, the number of components is two, and there are also two phases, solution and vapour. Thus $r = 2$ and $n = 2$ and two of the three variables, pressure, temperature and concentration of the solution, are, by the phase rule, independent. Thus, if we fix the temperature and concentration, the solution has a definite vapour pressure.

9. Osmotic pressure.—Certain membranes have the property of allowing water, but not dissolved material, to pass through their walls. Such a membrane is said to be *semi-permeable*, as, for example, one formed by the interaction of copper sulphate and potassium ferrocyanide. The precipitated cupric ferrocyanide is permeable by water but not by sugar. The film is mechanically weak, but if a porous pot containing copper sulphate stands in a solution of potassium ferrocyanide, the chemical action and precipitation occur within the pores of the vessel, and thus the film receives the necessary support.

If a porous pot, impregnated by the membrane described above, contains a sugar solution and is immersed in water, the selective transmission causes an accumulation of water inside the vessel, with a consequent rise in the level of its liquid. The process ceases when a definite excess pressure is thereby produced. This pressure, which is called the *osmotic pressure*, clearly equals the difference of pressure which must initially be present on the solution side of the membrane if no osmotic action results. The walls of the membrane are continually receiving impacts from the water molecules on one side, and from a mixture of water and sugar molecules on the other. Since the sugar is not transmitted there will be an initial excess inflow of water. The accumulating excess pressure inside the vessel assists the escape of water from the inside, and tends to lessen the inflow. When a state of dynamic equilibrium is reached the exchange of molecules is balanced, and the rise of pressure ceases.

Pfeiffer* found that the osmotic pressure, P , was proportional to the concentration of the solution, *i.e.*, to the number of moles† of solute per unit volume of solvent. He also found that, at least

* *Osmotische Untersuchungen* (1877).

† A mole is a gram-molecule.

approximately, the osmotic pressure was proportional, for a given solution of constant strength, to the absolute temperature. Hence,

$$P \propto C, \text{ and } P \propto T,$$

or, combining these two laws,

$$P = CRT.$$

Van't Hoff * calculated the value of R from Pfeiffer's results for cane sugar, and obtained 8.41 joules per mole, compared with 8.36, the value of the gas constant. He suggested that the molecules of sugar in dilute solution produce the same pressure as they would if they were gaseous molecules filling the same space. While experimental work shows that the osmotic pressure of dilute solutions, as measured, is identical, within the limits of experimental error, with the gas pressure, as predicted by the van't Hoff formula, this is not so when the solutions begin to be moderately concentrated. Attempts † have been made to account for the behaviour under these conditions by applying gas equations such as that of van der Waals, viz., $\left(p + \frac{a}{v^2}\right)(v - b) = RT$.

Sackur ‡ used a modified form of van der Waals' equation which holds good, with considerable accuracy, up to very high concentrations. The equation is

$$P(V - b) = RT,$$

where P is the osmotic pressure, V the volume of solution containing 1 mole of solute, and b is a constant. Porter § has also advanced a theory of the osmotic pressure in concentrated solutions, and many other workers have investigated the properties of such solutions.

10. Vapour pressure of a solution.

— The vapour pressure of a solution is less than that of the pure solvent, the

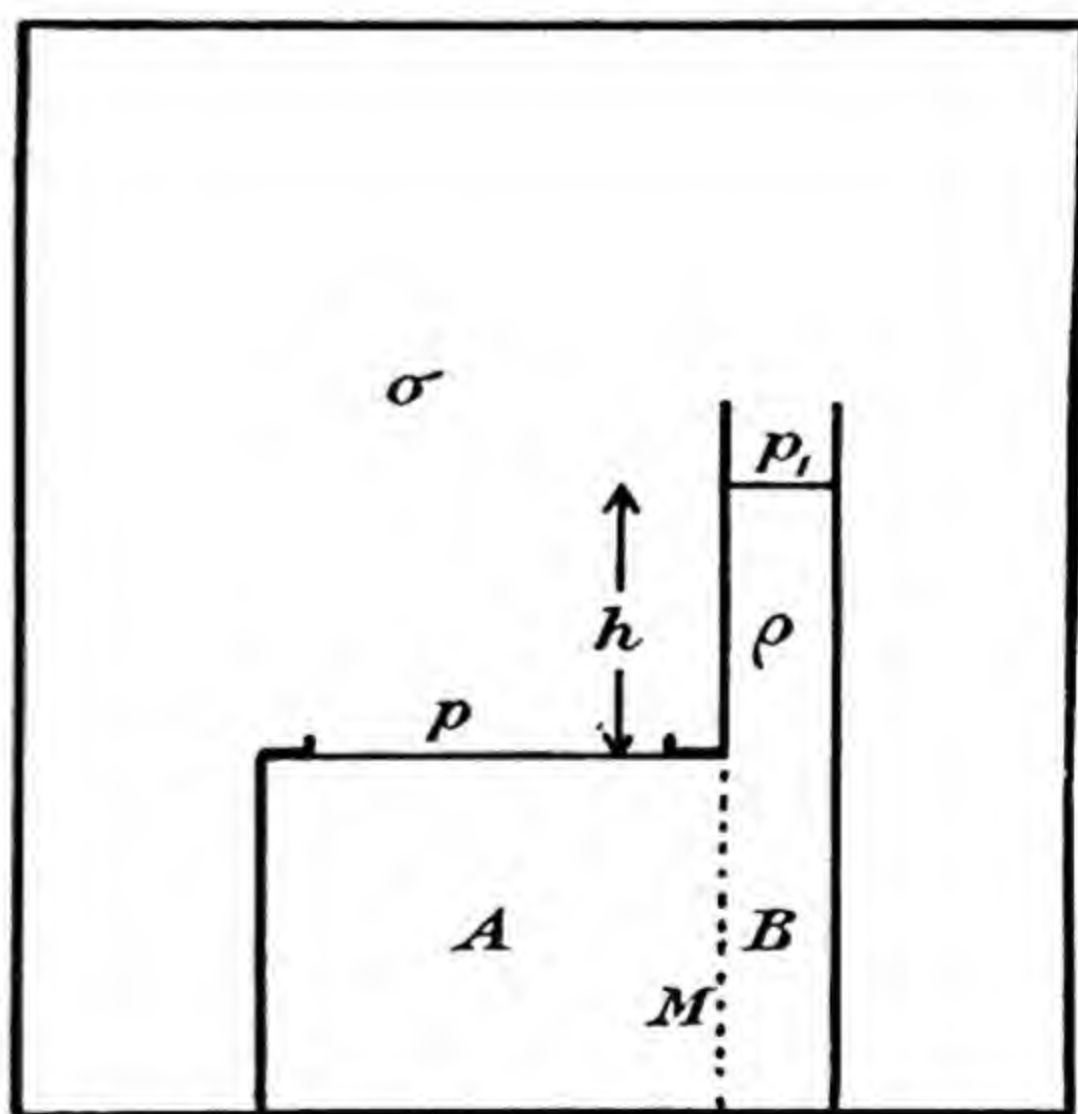


FIG. 1.—Vapour pressure of a solution.

* *Phil. Mag.*, 26, 81 (1888); *Berichte*, 27, 6 (1894).

† See Stern, *Zeits. phys. Chem.*, 81, 441 (1912).

‡ *Zeits. phys. Chem.*, 70, 477 (1910).

§ *Proc. Roy. Soc., A*, 79, 519, (1907), 80, 457 (1908).

lowering of the vapour pressure being determined as follows. Consider a vessel divided into two parts, A and B, by a semi-permeable membrane, M, as shown in Fig. 1. The former part contains pure solvent, the vapour pressure immediately over its surface being p , while B contains the solution whose vapour pressure is p_1 . The vessel is enclosed by another outer vessel containing, in addition to the liquids, only the vapour of density σ . Owing to osmosis the level of the liquid in B will be higher by an amount h than that in A, the difference in pressure on the two sides of the membrane being P , the osmotic pressure of the solution. Thus,

$$P = p_1 + g\rho h - p,$$

where ρ is the density of the solution. Since p and p_1 are pressures at a difference of level h in the vapour,

$$p = p_1 + g\sigma h.$$

Hence,
$$\frac{p - p_1}{\sigma} = \frac{P + p - p_1}{\rho},$$

or
$$p - p_1 = \frac{P\sigma}{\rho - \sigma} = \frac{P\sigma}{\rho}, \text{ approximately.} \quad (18)$$

If σ_0 is the vapour density under standard atmospheric pressure, p_0 ,

$$\sigma = \frac{\sigma_0 p}{p_0},$$

and
$$\frac{p - p_1}{p} = \frac{P\sigma_0}{p_0\rho} \text{ approximately.} \quad (19)$$

Since $p = nRT$, and $P = n'RT$, where n is the number of moles of vapour per unit volume, and n' the number of moles of solute per unit volume, we have from equation (18),

$$\frac{p - p_1}{p} = \frac{n'\sigma}{n\rho}.$$

Assuming that the density of the dilute solution is equal to that of the solvent,

$$\frac{\sigma}{\rho} = \frac{n}{n''},$$

where n'' is the number of moles of solvent per unit volume. Thus,

$$\frac{p - p_1}{p} = \frac{n'}{n''} = \frac{1}{N}, \quad (20)$$

N being the number of moles of solvent containing one mole of solute, and the relative lowering of the vapour pressure is independent of the nature of the solvent and solute.

We have assumed that the vapour density is uniform, but this assumption is justified only if the vapour column height, h , is small, *i.e.*, if the concentration of the solution is low. When this is not so we must write,

$$\delta p = -g\sigma \cdot \delta h,$$

so that

$$\delta h = -\frac{p_0}{g\sigma_0} \cdot \frac{\delta p}{p}.$$

Integrating,

$$h = \frac{p_0}{g\sigma_0} \cdot \log \frac{p}{p_1},$$

or, substituting for h in the relation $P = g\rho h$,

$$\log \frac{p}{p_1} = \frac{P\sigma_0}{p_0\rho} \quad \quad \quad (21)$$

This gives the necessary relation between the osmotic pressure and the lowering of the vapour pressure of a solution, and is independent of any assumption as to the physical nature of osmotic pressure.

11. Boiling-point temperature of a solution.—The vapour pressure of a solution is lower than that of the pure solvent, and therefore the boiling-point temperature of a solution is higher than that of the solvent. The elevation may be evaluated as follows: Fig. 2 represents a closed vessel divided into two compartments, A and B, by a semi-permeable membrane. The upper half of each chamber contains only the vapour of the solvent, while A has also a quantity of a solution at a temperature $T + \delta T$, and B some solvent at a temperature T . Let these temperatures, at which the vapour pressures are equal, be the boiling-point temperatures, and suppose that the following reversible cycle is performed:—

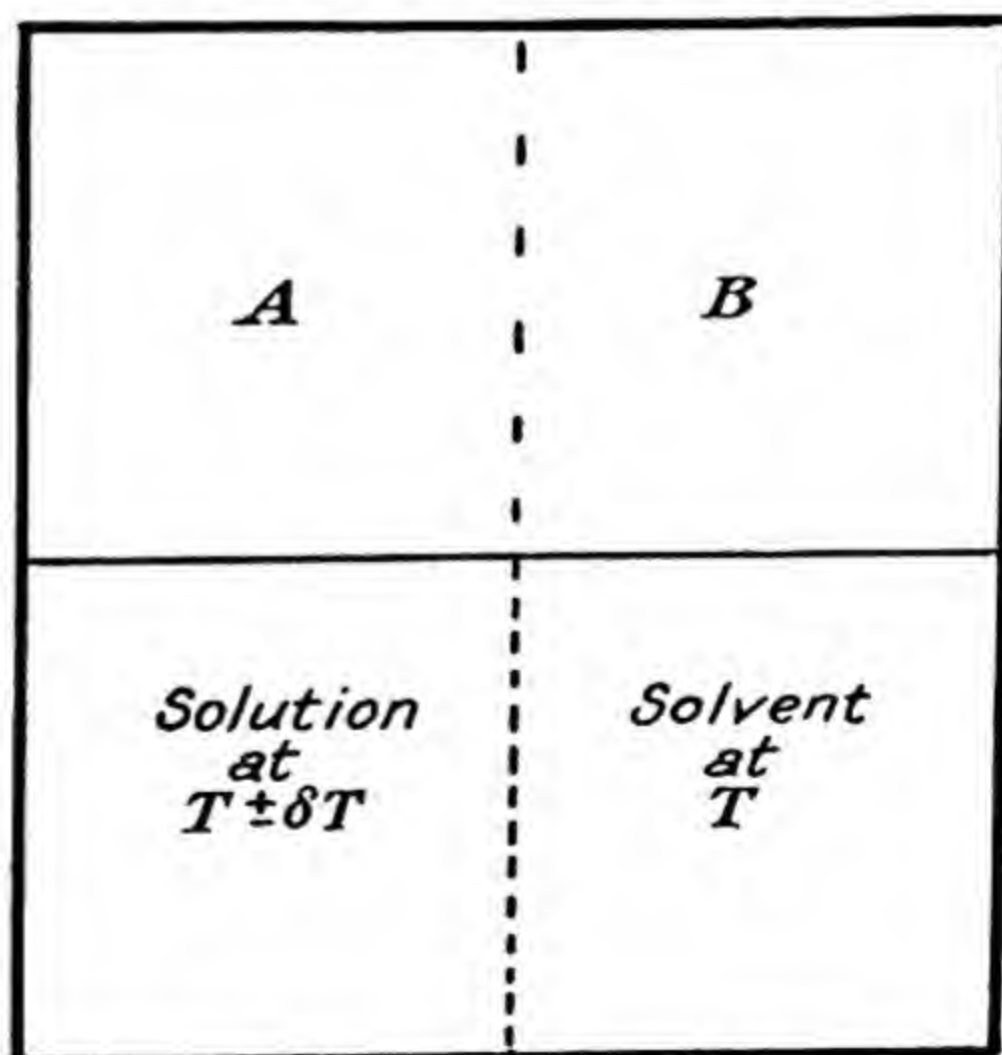


FIG. 2.—Boiling-point and freezing-point temperatures of a solution.

12. Freezing-point temperature of a solution.—When a solution freezes, it is in equilibrium both with the ice that freezes out and with the vapour, and the three phases exist at the same pressure. Since the vapour pressure of a solution is less than that of the pure solvent at the same temperature, the freezing-point of the solution is lower than that of the solvent.

In Fig. 2 let T and $T - \delta T$ represent corresponding freezing-point temperatures, and suppose that a reversible cycle is performed as follows :—

(i) Force a volume, v , of the solvent from B to A. The work done will be Pv , P being as before the osmotic pressure.

(ii) Freeze this quantity of solvent in A. The heat liberated is $\rho v L_1$, where L_1 is the latent heat of fusion at the temperature $T - \delta T$.

(iii) Transfer the solid thus formed from A to B.

(iv) Allow the solid to melt. During this process it absorbs heat equal to $\rho v L$, L being the latent heat of fusion at the temperature T . Then from the two laws of thermodynamics,

$$\frac{\rho v L_1}{T - \delta T} = \frac{\rho v L}{T} = \frac{Pv}{\delta T},$$

or, as in section (11) the depression of the freezing-point temperature is given by

$$\delta T = \frac{RT^2}{NL}, \quad . \quad . \quad . \quad . \quad (24)$$

where L is now the latent heat of fusion per mole of the solvent. The depression of the freezing-point temperature is the same for all non-dissociating substances dissolved in the same solvent, provided that the concentration, expressed in moles of solute per mole of solvent, remains the same. The *molecular depression* for such substances in 100 grams of water is thus,

$$\delta T = \frac{8.315 \times 10^7 \times 273^2}{\frac{100}{18} \times 80 \times 4.18 \times 10^7 \times 18} = 18.58^\circ \text{C}.$$

For a solution of n moles of solute per 100 moles of solvent,

$$\delta T = \frac{nRT^2}{100L}. \quad . \quad . \quad . \quad . \quad (25)$$

This expression has been verified for different solvents.

13. Molecular weights.—The molecular weight of a substance, which does not dissociate when dissolved in a solvent, can

be determined by measuring the boiling-point temperature elevation, or the freezing-point temperature depression, of such a solution of known concentration. Thus, if δT is the observed elevation, or depression, in these two cases, of a solution containing m grams of solute per 100 grams of solvent, and if M is the molecular weight of the solute, $n = \frac{m}{M}$, so that from equation (25),

$$\delta T = \frac{mRT^2}{100 ML} \quad (26)$$

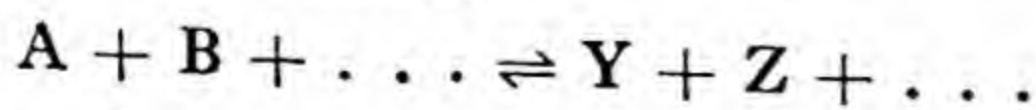
Thus M may be determined.

It must be emphasised that all of the results, deduced from osmotic pressure considerations, assume that there is no dissociation of the solute when it is dissolved in the solvent. On dissolving, the molecules of a solute may dissociate into two or more particles, and then the osmotic pressure produced is greater than it would be in the absence of such dissociation.

Organic solutes dissolved in water give osmotic effects which agree with van't Hoff's theory, these effects depending upon the number and not upon the nature of the dissolved molecules. When experiments yield abnormally low values, it follows that the number of solute particles is less than that indicated by the chemical formula, and it is natural to suppose that aggregation has occurred. On the other hand, large values indicate dissociation, and the degree of dissociation may be determined by measuring the osmotic pressure effects.

14. The law of mass action.—In a homogeneous system, *i.e.*, one which has the same physical and chemical nature at every point, it is possible to make a reaction proceed in either direction. In general, the equilibrium state is associated with definite temperature and pressure conditions, any change in these conditions causing a shift in the equilibrium state. Great precautions must be taken before one can regard any system as having arrived at this state; the fact that no material change can be observed, even after the lapse of a long period, is by no means sufficient to show that there is equilibrium.

Suppose that the molecular species A , B , *etc.*, have been brought together in a homogeneous system, and react upon each other according to the scheme,



Let the reacting substances be gaseous, and their concentrations, C_A , C_B , *etc.*, moles per c.c. The appearance of new molecules,

or atoms, of a given species during any process of chemical change will give rise to an increase in the available energy, and this increase will involve two terms * ; one giving the work, a , done in forming the molecule, or atom, at the chosen temperature and a standard pressure, and the other, expressing the work required to transform, under isothermal conditions, the new substance from the standard pressure to that at which the system exists. As shown in section (1) this second term will be of the form $RT \log \frac{p}{p_0}$, where p is the actual pressure, and p_0 the standard pressure. Hence we may write the increase of available energy of the system in the form,

$$a + RT \log bC,$$

where C , the final concentration of a given species, is proportional to p , and a is a function of the temperature T , b being a constant which depends on the standard of reference. It expresses the dilution of the particles at the standard pressure and at the existing temperature.

A reaction in a system involves the disappearance, by breaking up, of molecules of some species present, and the appearance of molecules of other types to an equivalent extent, so that if n_A , n_B , etc., represent the numbers of moles which are involved in the reaction, the increase, $\delta\psi$, in the free energy, is given by

$$\delta\psi = n_A(a_A + RT \log b_A C'_A) + n_B(a_B + RT \log b_B C'_B) + \dots, \quad (27)$$

where C'_A , C'_B , etc., are the arbitrary concentrations of the species, and n_A , n_B , etc., are reckoned *positive* if they *appear* and *negative* if they *disappear*.

When the equilibrium state is attained, the change of free energy, arising from a further transformation, must vanish. Hence $\delta\psi = 0$, and from equation (27),

$$RT \log (C_A^{n_A} \cdot C_B^{n_B} \dots) = - [n_A a_A + n_B a_B + \dots + RT(\log b_A^{n_A} \cdot b_B^{n_B} \dots)], \quad (28)$$

where C_A , C_B , etc., are the concentrations at the equilibrium state. Thus, if we write

$$RT \log K = - [n_A a_A + n_B a_B + \dots + RT(\log b_A^{n_A} \cdot b_B^{n_B} \dots)],$$

we have

$$C_A^{n_A} \cdot C_B^{n_B} \cdot C_C^{n_C} \dots = K. \quad (29)$$

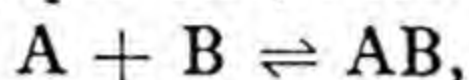
K is known as the *equilibrium constant*. It is independent of the concentrations, and depends only upon the temperature. By means of this last equation the value of K for any reaction, gaseous

* See Larmor, *Phil. Trans.*, A, 190, 276 (1897).

or in solution, at a constant pressure and temperature, can be determined by measuring the concentrations, in moles per unit volume at the equilibrium state, of all the reacting substances.

The relationship expressed by equation (29) is known as the *law of mass action*, and it has been applied to all types of reversible actions. We shall use it a great deal in studying the properties of dilute solutions.

If the reaction is a simple one, such as



then $n_A = n_B = 1$ and $n_{AB} = -1$, so that

$$\frac{C_A \cdot C_B}{C_{AB}} = K. \quad . \quad . \quad . \quad (30)$$

15. Variation of the equilibrium constant with temperature.—If the concentrations of the various species present in a system do not correspond to those existing at the equilibrium state, the free energy, per mole, in reaching this state is given by equation (27). Utilising equations (28) and (29) we may write for $\delta\psi$,

$$\delta\psi = -RT \log K + RT \Sigma n \log C', \quad . \quad . \quad (31)$$

where $\Sigma n \log C'$ is equal to $n_A \log C_A' + n_B \log C_B' \dots$. If $\delta\psi_0$ is the free energy change when each substance is in its standard state, we have

$$\left. \begin{array}{l} \delta\psi_0 = -RT \log K. \\ \delta\psi = \delta\psi_0 + RT \Sigma n \log C'. \end{array} \right\} \quad . \quad . \quad (32)$$

Differentiating equation (31) with respect to temperature, and remembering that $\Sigma n \log C'$ is independent of the temperature,

$$\frac{\partial}{\partial T} \delta\psi = -R \log K - RT \frac{\partial}{\partial T} \log K + R \Sigma n \log C'.$$

Also from equation (31),

$$\frac{\delta\psi}{T} = -R \log K + R \Sigma n \log C'.$$

$$\text{Thus,} \quad \frac{\partial}{\partial T} \delta\psi = \frac{\delta\psi}{T} - RT \frac{\partial}{\partial T} \log K,$$

$$\text{or} \quad T \frac{\partial}{\partial T} \delta\psi = \delta\psi - RT^2 \frac{\partial}{\partial T} \log K.$$

Hence from equation (5),

$$\delta E = RT^2 \frac{\partial}{\partial T} \log K.$$

If the small amount of reaction, represented by the δ , occurs so that no mechanical work is done on, or by, the system, we have from the first law of thermodynamics, $\delta E = \delta Q$, the amount of heat taken *into* the system ; so that if we represent by $-H_v$ the heat *evolved*, per mole, by the reaction at constant volume, then $\delta Q = H_v$ and thus,

$$\frac{H_v}{RT^2} = \left(\frac{\partial}{\partial T} \log K \right)_r, \quad . \quad . \quad . \quad (33)$$

— H_v is known as the *heat of dissociation at constant volume*. Most reactions, however, occur at constant pressure, and in this case,

$$\frac{H_p}{RT^2} = \left(\frac{\partial}{\partial T} \log K \right)_p, \quad . \quad . \quad . \quad (33a)$$

— H_p being the *heat of dissociation at constant pressure*. It will be seen that the heat of dissociation is *positive* if heat is *evolved* when the action proceeds in the direction indicated by equation (28).

The relationships expressed by equations (33) and (33a) are usually called the *Equations of the Isochores of Reaction*. They are of fundamental importance, and hold for homogeneous and heterogeneous gas reactions, as well as for solutions. Both H_v and H_p may be measured by means of calorimetry experiments, and thus the variation in the value of the equilibrium constant with temperature may be determined at various temperatures. We see from equations (29) and (33) that an *increase* in the temperature causes the equilibrium to be displaced in the direction corresponding to *absorption* of heat from outside the system.

16. Gibbs' adsorption equation.—When dealing with capillarity phenomena we shall have occasion to consider the properties of the interface at which two phases meet. Gibbs* pointed out that in addition to those variables already considered when dealing with the phase rule, *viz.*, temperature, pressure and concentration, one must also take into account the interfacial surface areas. From thermodynamical considerations he showed that if a dissolved substance had the property of lowering the surface tension of a solution at its interface, the substance would exist at a higher concentration in this interfacial layer than in the bulk of the solution.

Generally speaking, one regards the boundary separating two phases, such as liquid and vapour, simply as a geometrical surface upon one side of which there is a phase of uniform properties, and on the other a second phase, everywhere distinct from the

* *Scientific Papers*, vol. 2.

first and homogeneous in itself. Actually this is not the case, nor do the contiguous layers shade, as it were, rapidly, but continuously, one into the other. We must regard the boundary as a film or lamina of finite, though minute thickness, consisting of an entirely different phase with definite and measurable properties. With solutions the composition of the interface phase is different from that of the solution in bulk. The interfacial energy of all interfaces must be a minimum, and with pure liquids the surface tension, S , is constant. Thus, the energy can decrease only by an area contraction. This is not so with solutions, for the surface tension varies with concentration, and the possibility exists that S tends to a minimum value with changing concentration. To bring this about the surface layer must be more dilute than the remainder of the solution, if S increases with concentration. On the other hand, if S decreases as the concentration is raised, the dissolved substance will collect in the surface layer. This impoverishment or enrichment of the surface phase does not continue indefinitely. A point is reached at which the action is balanced by a counter movement due to diffusion. The excess or deficiency of the solute in the superficial phase may be calculated by means of Gibbs' equation.

Consider a closed surface drawn about the portion of the interface at which the conditions are to be investigated. Let it contain parts of the two homogeneous phases, and cut the non-homogeneous parts normally to the interface. The actual volume contained within this enclosure thus formed is divided into two parts by a dividing surface, drawn parallel to, and sensibly coincident with, the actual surface. The amounts of internal energy, entropy and masses of the components within the enclosure will differ from those amounts which would be present if the homogeneous phases extended, without change, up to the dividing surface. Let these differences be E_A , ϕ_A and m_1 , etc., respectively. Then the variation in E_A for a small change, δA , in the area of the dividing surface, is, from equation (14),

$$\delta E_A = T\delta\phi_A + S\delta A + \mathbf{F}_1\delta m_1 + \dots, \quad (34)$$

where $S\delta A$ is equivalent to $-p\delta v$, the work done on the surface in stretching it under isothermal conditions, and the masses in the superficial layer are assumed to increase simultaneously, so that the concentrations of these masses remain constant. If these conditions hold, and the surface area is increased by unit area, we have

$$E' = T\phi' + S + \mathbf{F}_1C_1 + \dots, \quad (35)$$

E' , ϕ' , C_1 representing the *excess* amounts of internal energy, entropy and masses, respectively, per unit area of the dividing surface, *i.e.*, they represent what we may term the *surface densities* of these physical quantities in the dividing surface. Differentiating equation (35), and utilising equation (14) in the result, we have

$$\phi'\delta T + \delta S + C_1\delta F_1 + \dots = 0. \quad (36)$$

If the temperature remains constant, and there are two components,

$$\delta S = -C_1\delta F_1 - C_2\delta F_2,$$

which reduces to

$$\delta S = -C_2\delta F_2, \quad (37)$$

if C_1 is negligible compared with C_2 .

From equation (17)

$$F_2 = \frac{dF}{dm_2}.$$

Hence we see that F_2 is the amount of work necessary to introduce unit mass of one component, and, therefore, if the solution is dilute, this work is proportional to $RT \log P$, where P is the osmotic pressure exerted by the component. Thus we may write F_2 in the form,

$$F_2 = a + RT \log C, \quad (38)$$

where a is a constant, and C is the final concentration in moles of the component, *i.e.*, the actual concentration in the bulk of the solution. Hence,

$$\delta S = -C_2 RT \delta(\log C),$$

$$\text{or} \quad C_2 = -\frac{1}{RT} \cdot \frac{\partial S}{\partial(\log C)} = -\frac{C}{RT} \cdot \frac{\partial S}{\partial C}, \quad (39)$$

where C_2 is the quantity of solute transferred from the interior of the liquid to the interface, and is positive, or negative, according as the addition of solute decreases, or raises, the surface tension of the solution. In other words, if there are two components in a liquid, and the surface tension is increased when the concentration of one component is raised, then the surface concentration of that component, relative to the other, is lowered. It will be noted that C is the actual concentration of the component in the bulk of the solution, due allowance being made for the fact that in the surface layer the component is present to a greater or less extent than in the bulk.

Gibbs' theorem, embodied in equation (39), has been verified

experimentally, and it covers a wide field. Thus, the addition of a solute to a solvent will cause marked changes in the composition of the surface phase if the solvent and solution possess different surface tensions.

This surface concentration, or tendency for molecules to pass to, and remain at, an interface, is identified with the phenomenon of *adsorption*.

BIBLIOGRAPHY.

- Arrhenius, Zeits. phys. Chem., **3**, 115 (1889).
Bertholet et Péan de St.-Gilles, Ann. Chim. Phys., **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).
Gibbs, Equilibre des Systèmes Chimiques, Paris (1899), Scientific Papers.
Groves, Phil. Trans., A, **137**, 1 (1847).
Guldberg and Waage, Etudes sur les affinités chimiques, Christiania (1867).
Morse and Frazer, Amer. Chem. Journal (1901-12).
Nernst, The New Heat Theorem (1926).
Raoult, Comptes Rendus, **103**, 1125 (1886); **104**, 1430 (1887); **94**, 1517 (1882); **95**, 188, 1030 (1882); Zeits. phys. Chem., **2**, 353 (1888); Ann. de Chim. et de Phys., **28**, 137 (1883).
Soret, Archives des sciences phys. et nat., **11**, p. 48; Ann. de Chim. et de Phys., **22**, 293 (1877).
van der Waals, Die Kontinuität des gasförmigen und flüssigen Zustands, Teile 1. u. 11., Leipzig (1899).

CHAPTER II.

ELECTROLYSIS.

17. Introduction.—Electrical conductivity is a property common to all substances, and an electric current passing through matter may, or may not, be accompanied by a simultaneous transfer of the matter. Metals conduct without such transference, but material effects are associated with the conduction process in certain substances, termed *electrolytes*. Metallic conductors are characterised by having relatively high conductivities, the conductivity decreasing as the temperature is raised. Electrolytes show the opposite temperature effect. Metallic and electrolytic conduction are not, however, unrelated, as sometimes these two processes take place more or less simultaneously, and the current is conducted partly by one process, and in part by the other.

There are two classes of electrolytic conductors, *viz.*, fused salts, which conduct in the pure state, and secondly, substances which conduct when they are dissolved in non-conducting solvents, such solutions being termed *electrolytic solutions*. Both solute and solvent may be very poor conductors as, for example, pure hydrochloric acid and water, but if these two substances are mixed, the resulting solution possesses considerable conductivity. This property of forming electrolytic solutions is not restricted to water, but is common to many solvents, including the alcohols, liquid sulphur dioxide and many others. It seems to depend upon the *dielectric constant* of the solvent. On the whole, the value of the conductivity of salt solutions becomes greater as the *specific inductive capacity* of the solvent increases, but the power of conducting electricity is never completely lost, even if the specific inductive capacity of the solvent has a very low value.

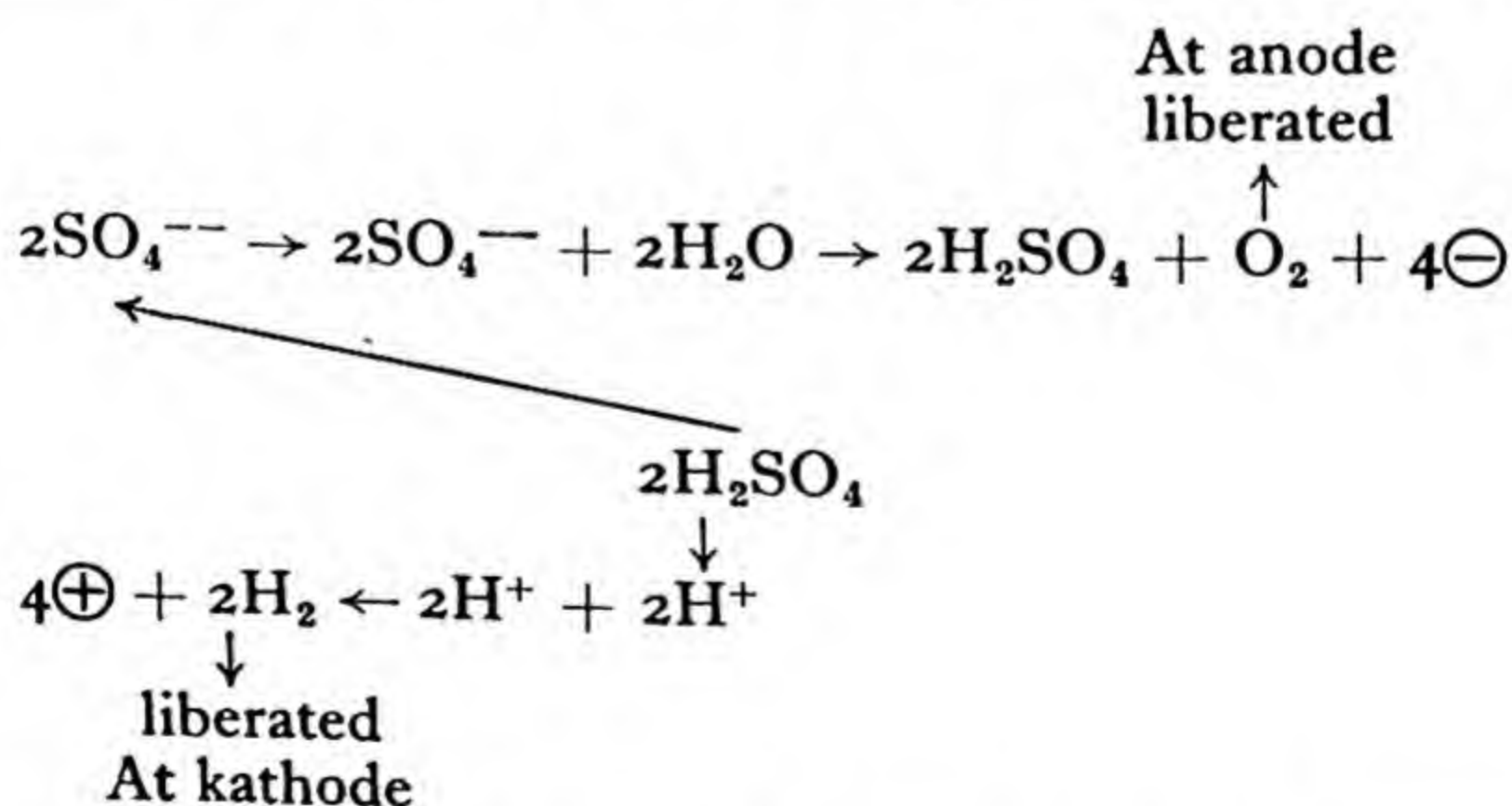
18. Electrolysis.—Electrolytic solutions give rise to many reactions and phenomena which are not shown by any other class of substances. If an electric current is passed between platinum plates, immersed in a dilute sulphuric acid solution, the latter appears to suffer chemical decomposition to some extent, oxygen being liberated at the *anode* and hydrogen at the *kathode*.* This phenomenon is termed *electrolysis*.

* That electrode, by means of which the current enters a solution, is termed the anode, and the other electrode the kathode.

Since sulphuric acid, in the pure state, and water are non-conductors, it is assumed that the acid in aqueous solution differs in some manner from its nature in the pure state. The molecule of acid is considered to consist of two parts, one, hydrogen, bearing positive electricity, and the other, the radical SO_4 , carrying negative electricity, these electrical charges being equal, so that on the whole the molecule is neutral. Atoms and radicals which carry electrical charges in this manner are termed *ions*. Although the sulphuric acid molecule, in the absence of solvents, is very stable, it is readily dissociated, or ionised, into its constituent ions in the presence of certain solvents, particularly water, the dissociation being represented by the equation,



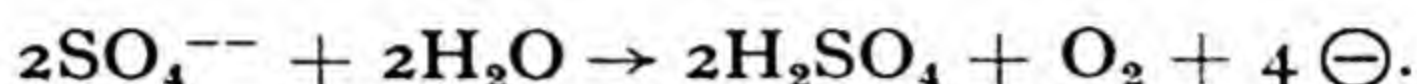
The symbol H^+ stands for a hydrogen atom carrying one unit of positive electrical charge, this hydrogen ion being often termed a *hydrion*. The radical ion SO_4^{--} carries two units of negative electrical charge, the actual unit of electrical charge being that associated with the electron. It is evident that if these ions exist throughout the bulk of the solution, an applied potential difference will cause the negatively charged ions, termed the *anions*, to move towards the anode, while the positively charged ions, *kations*, will migrate towards the kathode. We may therefore represent the electrolysis of an aqueous solution of sulphuric acid by the scheme,



where $4\oplus$ and $4\ominus$ represent the liberation of four units of positive, and four units of negative electrical charge, respectively, at the appropriate electrodes.

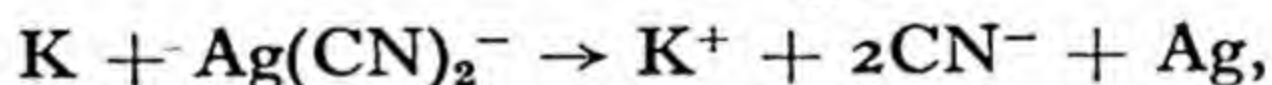
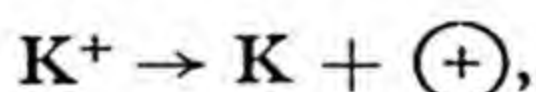
Thus we see that the constituents of water are liberated in the same proportion, by volume, as they exist in water, and, for this reason, the phenomenon is often erroneously referred to as the

electrolysis of water. It will be noted that the oxygen is a product of the secondary reaction between the SO_4^{--} ion and water. If copper sulphate solution is substituted for the acid, copper is deposited upon the kathode, which thus becomes electroplated, and oxygen is again liberated in the immediate neighbourhood of the anode, the solution round about this electrode developing acidity according to the reaction :—

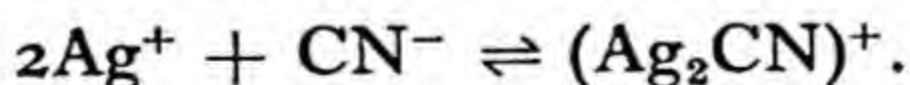
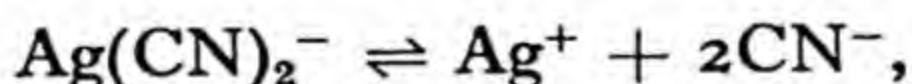


With a sodium hydroxide solution the sodium ions, deprived of their charge, react with the water in the vicinity of the kathode, producing sodium hydroxide and hydrogen gas.

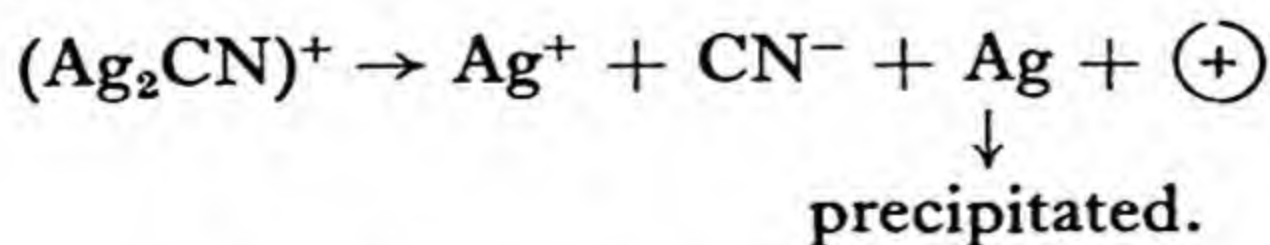
Except in a few cases, an element, or radical, if present in a solution, is always deposited at the same electrode from whatever compound it comes, but a study of the products of electrolysis does not necessarily indicate the ions actually involved in the passage of electricity through the electrolyte. For example, the electrolysis of an aqueous solution of potassium, or sodium, silver cyanide is a complicated process, and the nature of the actual ions present in the solution, which take part in the process, is not known with any degree of certainty. It was assumed, formerly, that the alkali metal formed the kation, and the complex radical, $\text{Ag}(\text{CN})_2^-$, the anion. On passing an electric current, it was supposed that the alkali-metal ion was first discharged at the kathode, and the sodium or potassium thus produced then reacted with the argentocyanide ions to produce silver, thus,



the silver being precipitated as the result of a secondary reaction. Glasstone,* however, has suggested that ions such as $(\text{Ag}_2\text{CN})^+$ and $(\text{Ag}_3\text{CN})^{++}$ may exist in solution, being formed thus,



So that at the kathode we have



* *Jour. Chem. Soc.*, 132, 690 (1929).

Hittorf * found that with platinic chloride solutions platinum was deposited at the anode, while Kohlrausch † noted that with an aqueous solution of this salt nothing apparently happened at the kathode, if small current densities were used, whereas if the current density was increased, a grey deposit was formed on the electrode.

A concentrated solution of sodium acetate, when electrolysed, gives rise to hydrogen gas at the kathode and a mixture of ethane and carbon dioxide at the anode, the hydrogen coming from the secondary reaction between sodium and water.

Another interesting case of electrolysis is that of hydrochloric acid solution. If the solution is weak, and a small current density is used, oxygen appears at the anode, instead of the expected chlorine. To explain this fact it must be remembered that although ions may be present in the immediate vicinity of an electrode, a certain potential difference, known as the *deposition potential*, which varies with the nature of the ion, must be applied to deposit these ions. Obviously those ions having the smallest deposition-potential value are the first to be deposited. Water is always slightly dissociated into its constituent ions, H^+ and OH^- , and since OH^- has a smaller deposition potential than that of Cl^- the former is deposited in preference, as it were, to the Cl^- . If the rate of supply of the OH^- ions is equal to their rate of deposition, it is evident that little, if any, chlorine will appear. This is so with weak solutions and small current densities. If both the concentration of the solution and the current density are raised, then chlorine is liberated in addition to the oxygen gas.

The examples quoted above indicate that a molecule of an electrolyte may dissociate into two or more ions, the actual number of ions depending upon the type of electrolyte. The molecule of a *binary* electrolyte, such as KCl , gives rise to two ions, while the molecule of a *tertiary* electrolyte such as H_2SO_4 may dissociate into three ions. If both ions formed from the molecule of an electrolyte are univalent, the electrolyte is said to be *uni-univalent*, *bi-bivalent* if both are bivalent, and *uni-bivalent* if the kation is univalent and the anion bivalent.

19. Faraday's law of electrolysis.—The earliest systematic study of electrolysis was made by Faraday,‡ and electrolysing acidulated water he found that the amount of decomposition was proportional to the quantity of electricity passed through the solution. He then showed that the same law was true for solu-

* *Pogg. Ann.*, 106, 517 (1859).

† *Wied. Ann.*, 63, 423 (1897).

‡ *Experimental Researches* (1833).

tions of various metallic salts, and also for salts in a state of fusion. In all cases the weight of material deposited was always the same for identical quantities of electricity, and was independent of current strength, size of electrodes and other variables.

In addition, he also found that the mass of ion liberated by a definite quantity of electricity was proportional to its chemical equivalent. For example, if the same quantity of electricity is passed through different solutions from which the following ions, hydrogen, oxygen, silver and chlorine, may be deposited, then for every 1 gram of hydrogen liberated, there are 8 grams of oxygen, 108 grams of silver, and 35.5 grams of chlorine set free at the appropriate electrodes.

These two laws of electrolysis may be incorporated in the equation,

$$w = zQ, \quad . \quad . \quad . \quad . \quad (40)$$

where w is the weight, in grams, of the ion deposited at the electrode during the passage of Q coulombs of electricity, and z , termed the *electro-chemical equivalent* of the ion, is the weight, in grams, of the ion deposited per coulomb. This equation implies that no current flows without a corresponding amount of deposition at the electrodes, *i.e.*, there is no leakage of the current unaccompanied by the transference of matter.

20. Voltameters.—Assuming the truth of Faraday's law of electrolysis, equation (40) gives a method of measuring the quantity of electricity which has passed through an electrolytic solution in a given time, and hence of measuring the average current. An electrolytic cell used in this manner is termed a *voltameter*. The oldest of these instruments is of the electrolytic gas type in which hydrogen and oxygen are separated and collected, either singly in calibrated tubes, or together in one tube. Formerly, the electrolyte employed was dilute sulphuric acid, but secondary reactions arise at the expense of the oxygen, and sulphuric acid is now replaced by phosphoric acid, or potassium and barium hydroxides. The gas volume must be reduced to normal temperature and pressure, due allowance being made for the water vapour pressure. On account of the inaccuracies of this type of voltameter it has now been superseded by the silver and copper voltameters.

In one type of copper voltameter, Fig. 3, the anode consists of two copper plates, AA, fixed in a circular disc of wood or ebonite, and the kathode, K, of copper, may be removed for weighing. The solution contains about 20 to 25 grams of crystallised copper

sulphate to 80 grams of water, together with 1 per cent. of concentrated sulphuric acid. The weight of copper deposited during a measured time interval is determined and, knowing the electrochemical equivalent of copper, the average current during the experiment is calculated with the aid of equation (40).

For accurate work the silver voltameter is preferred; in fact, the *international ampere* is defined as *that unvarying electric current which, when passed through a solution of silver nitrate in water, in accordance with certain specifications, deposits silver at the rate of 0.00111800 of a gram per second*. The electrolyte must

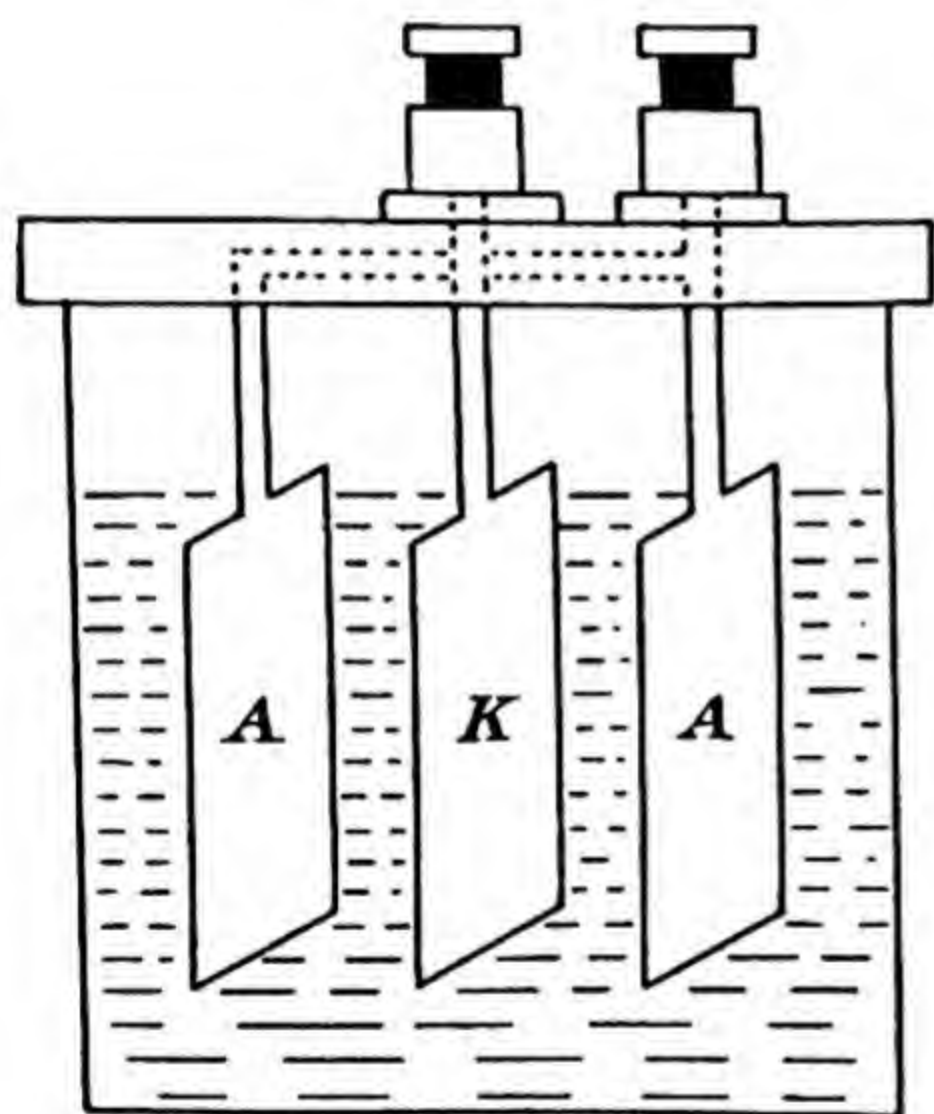


FIG. 3.—Copper voltameter.

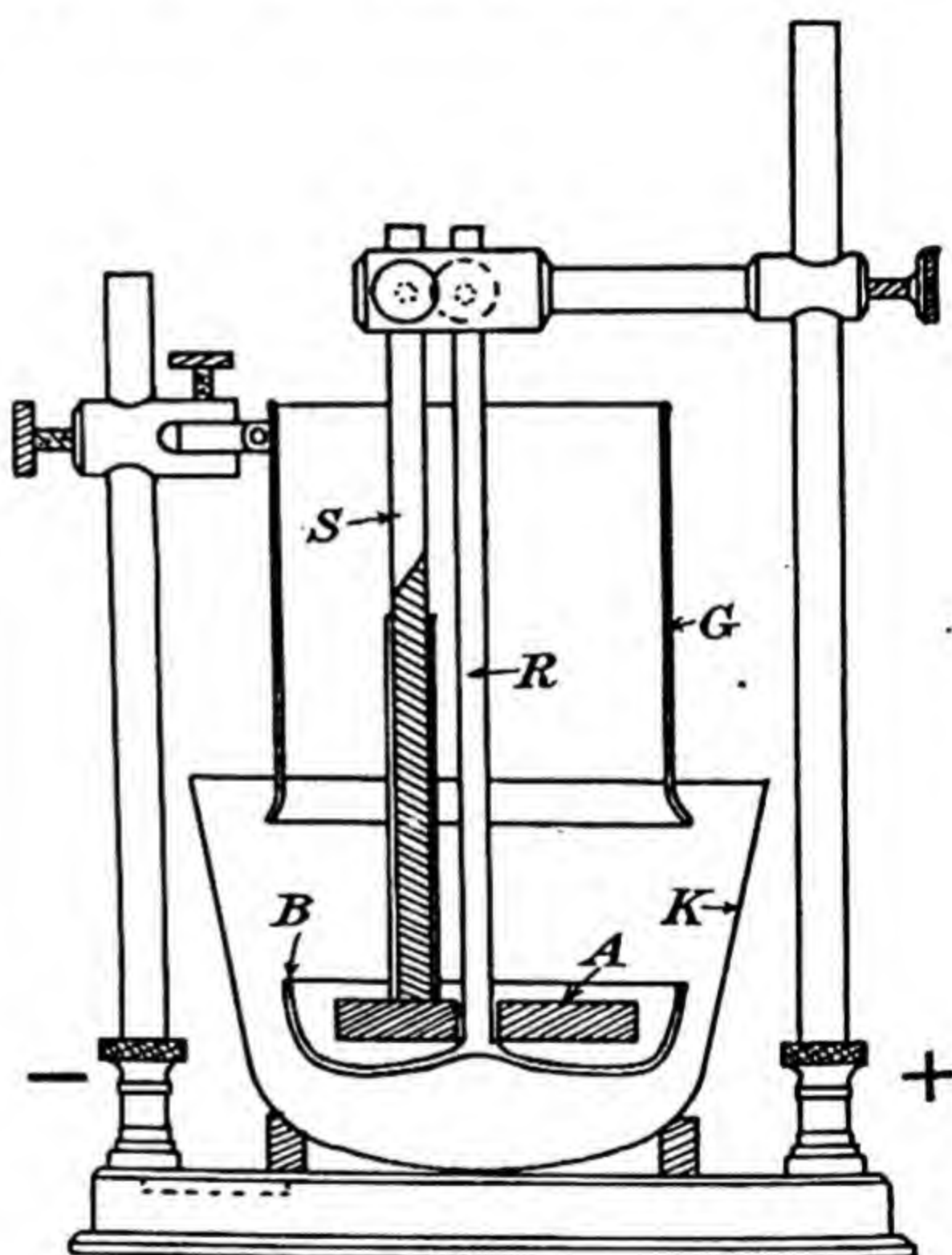


FIG. 4.—Silver voltameter. (Smith type.)

consist of a solution of from 15 to 20 parts by weight of silver nitrate in 100 parts of distilled water, the anode being of silver and the kathode preferably of platinum. The current density at the anode should not exceed 0.2 amp. per sq. cm., and at the kathode 0.02 amp. per sq. cm. Care must be taken that no particles, which may become mechanically detached from the anode, reach the kathode. It has been found that if the electrolyte contains oxide, carbonate, chloride or hyponitrite, the mass deposited is heavier than that set free from a pure solution of the nitrate.

The Smith type of voltameter is the one usually preferred in standard measurements. The anode A, Fig. 4, is in the form of a silver disc, coated with electrolytically deposited silver. This disc is contained in a shallow glass basin, B, with a ground edge, the basin being supported by means of a glass rod, R, passing through a hole in the centre of the disc. A glass cylinder, G, the lower end of which is ground, fits over the basin, and is used before and after the electrolysis to separate the electrolyte into two parts. A silver rod, S, supports the silver disc, and a glass tube fits over its lower end to prevent undue electrolysis of the rod. The kathode is a silver bowl, K. During electrolysis, the glass cylinder is raised, but its lower end is always immersed in the electrolyte. On the whole, however, the deposits obtained with all forms of voltameters agree, provided that the electrolyte is pure and does not become contaminated during electrolysis.

In the Rayleigh type of voltameter the anode consists of a plate, or rod, of pure silver wrapped in a filter paper, and the kathode is a platinum crucible. The filter paper prevents the black powder of disintegrated silver from falling upon the deposited silver in the crucible.

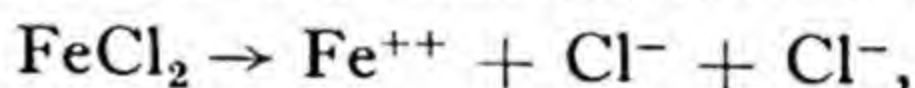
21. Theoretical considerations.—Assuming that the electric current passing through an electrolytic solution is due entirely to the ions, the value of the current is proportional to the number of ions, and to the velocity with which they move when an electric force is applied to the solution. Ionisation of the dissolved molecules may be *spontaneous* or it may be produced by the electric field. If it is forced the rate of dissociation can be represented by $f_1(\mathbf{E})$ —a function of the applied potential difference. The ionic velocity must also be some function of \mathbf{E} , say $f_2(\mathbf{E})$, and therefore the electric current is proportional to $f_1(\mathbf{E}) \cdot f_2(\mathbf{E})$. This product is unlikely to be proportional to the first power of \mathbf{E} , as it should be if Ohm's law holds, as it does, for electrolytic solutions. Thus we conclude that ionisation is entirely spontaneous, and is brought about by the act of solution. The ions exist before any electric field is applied; the latter merely directs the ions towards their appropriate electrodes. If the ionisation is spontaneous, it may be *complete* or *partial*, and if partial, then it will be *permanent* or *intermittent*. Various experimental facts, which will be considered later, indicate that in general ionisation is not complete.

Consider a solution of definite concentration. The ions will share the kinetic energy of the molecules present, and will therefore travel from one place to another. During the course of their wanderings oppositely charged ions will collide and reunite to form

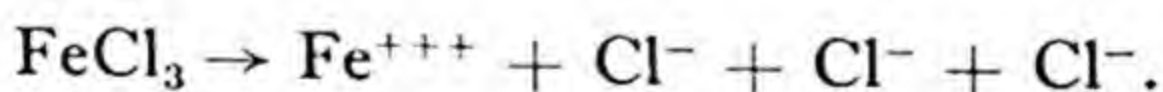
a molecule. But we must assume that there is equilibrium within the solution, the rate of ionisation being equal to this rate of recombination, so that for every molecule re-formed one must be ionised. In other words, the *partial ionisation* is *intermittent*.

The undissociated molecules do not contribute to the current, and other things being equal, a solution will have a smaller resistance, the larger the fraction of dissociated molecules present in the solution. The separation of an electrolyte into its constituents is entirely a spontaneous process accompanying the act of solution. It is neither a part of the electrolysis process, nor is it dependent in any manner upon the introduction of a potential difference within the solution. It is, however, a precursor of electrolysis. The ions Na^+ and Cl^- , for example, stand free in every part of a sodium chloride solution, and are directed by the applied potential difference to the kathode and anode, respectively. As these ions are conveyed to the electrodes, it is evident that the weight of ions deposited must be proportional to the quantity of electricity passing through the solution. This fact was discovered by Faraday long before any theory of electrolytic dissociation had been formulated.

It is very remarkable that similar ions may have different charges under different conditions ; thus the iron ion, produced by the dissociation of ferrous chloride, is divalent :—



while the iron ion, formed by the dissociation of ferric chloride, is trivalent :—



In general, the electrical charge upon an ion is by no means constant ; in fact, it varies with the valency of the ion.

Since equivalent weights of ions are deposited by the passage of the same quantity of electricity through solutions, we associate each gram equivalent of an ion with a definite charge, which is shown later to be 96,491 coulombs. The electricity is firmly bound to the ion, and can only be given up at the electrodes, the ion then ceasing to exist as such. It is easy to understand that equivalent quantities of different substances are charged with the same amount of electricity, for when solutions of two electrolytes are mixed, say calcium chloride, CaCl_2 , and sodium nitrate, NaNO_3 , partial exchange takes place, and there are formed sodium chloride, NaCl , and calcium nitrate, $\text{Ca}(\text{NO}_3)_2$. Now if one atom of calcium, *i.e.*, two equivalents, were not charged with the same quantity of electricity as two NO_3 radicals, or the two

sodium atoms originally combined with these, but had a greater positive charge, the molecules of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, would be positively, and the sodium chloride molecules negatively, charged, since the original solutions were electrically neutral. By means of physical or chemical processes the substances could be separated, and after this separation the solutions should be electrically charged. As not the slightest charge can be found on the solutions, it must be assumed that equivalent quantities of the various substances, *i.e.*, ions, have the same charge.

If we represent a dissolved salt by MX , where M and X refer to the metallic and radical parts, respectively, the passage of νF coulombs electrolyses $m + x$ grams of the solute, where ν is the valency of each ion, F the charge associated with 1 gram equivalent of a univalent ion,* and m and x are the atomic weights of M and X , respectively. Thus m grams of M , bearing νF coulombs of positive charge, will be deposited at the kathode and x grams of X at the anode, these latter ions conveying a negative charge of νF coulombs. This association of a definite charge with a definite mass of ion holds throughout the volume of the solution, and two streams of matter pass in opposite directions if a potential difference is applied.

The theory of *spontaneous electrolytic dissociation* is confirmed by other physical phenomena. It has been shown, previously, that equimolecular solutions of non-dissociating solutes give the same molecular depression of the freezing-point temperature, but a dilute aqueous solution of potassium chloride has a molecular depression which is practically double the normal value. It is necessary to infer, therefore, that the number of particles in the chloride solution is nearly double the number of dissolved molecules of salt. In other words, practically all of the molecules have dissociated into their constituent ions.

22. Electro-chemical equivalents.—The electro-chemical equivalent of an element may be calculated from known physical constants. Thus, the atomic weight of hydrogen is 1.0077, and if we assume that the hydrogen ion in solution carries the unit of electrical charge, *viz.*, 4.774×10^{-10} electrostatic unit, or 1.592×10^{-20} electromagnetic unit, this amount of charge passes to the kathode for every hydrogen ion deposited thereon. Hence the number of hydrogen atoms—ions deprived of their electric charge—liberated by the passage of unit electromagnetic charge is

$\frac{1}{1.592 \times 10^{-20}}$. The number of molecules in a mole of hydrogen,

* Now usually called the faraday.

i.e., the number of atoms in a gram-atom,* is 6.062×10^{23} , and since the mass of the hydrogen atom is 1.663×10^{-24} gram, the amount of hydrogen liberated by the passage of the unit electromagnetic charge is $\frac{1}{1.592 \times 10^{-20}} \times 1.663 \times 10^{-24} = 1.045 \times 10^{-4}$ gram, or the weight of hydrogen deposited at a kathode when 1 ampere flows through an electrolytic solution containing hydrogen

TABLE I.
ELECTRO-CHEMICAL EQUIVALENTS.

Element.	Atomic Weight.	Valency.	Electro-chemical Equivalent. Gram per Coulomb $\times 10^4$.
Barium	137.37	2	7.123
Bromine	79.916	1	8.287
Cadmium	112.41	2	5.829
Calcium	40.07	2	2.078
Chlorine	35.458	1	3.677
Cobalt	58.97	2	3.058
Copper (cupric)	63.57	2	3.296
" (cuprous)	63.57	1	6.592
Gold	197.2	3	6.817
Hydrogen	1.0077	1	0.104
Iodine	126.932	1	13.164
Iron (ferric)	55.84	3	1.930
" (ferrous)	55.84	2	2.895
Lead	207.20	2	10.743
Mercury (mercuric)	200.61	2	10.402
" (mercurous)	200.61	1	20.804
Nickel	58.69	2	3.043
Oxygen	16.00	2	0.830
Potassium	39.095	1	4.054
Silver	107.880	1	11.187
Sodium	22.997	1	2.385
Tin (stannic)	118.70	4	3.077
" (stannous)	118.70	2	6.155
Zinc	65.38	2	3.390

ions is 1.045×10^{-5} gram per second. This is the electro-chemical equivalent of hydrogen, and from it the electro-chemical equivalents of all the other ions may be calculated if their chemical equivalents are known. Thus, if A is the actual weight, in grams, of an ion, ν its valency and e_0 the unit of charge, *i.e.*, the charge associated with an electron,

$$z = \frac{A}{\nu e_0}.$$

* A gram-atom is the atomic weight in grams of an element.

If W is the atomic weight of an element,

$$z = \frac{W}{\nu F}$$

where F is the charge associated with 1 gram-equivalent * of an ion, and is equal to $6.062 \times 10^{23} \times 1.592 \times 10^{-20}$ electromagnetic units, or 96,491 coulombs.

The calculated values of the electro-chemical equivalents of some elements are given in Table I.

BIBLIOGRAPHY.

- Buff, Lieb. Ann., 85, 1 (1853); 94, 1 (1855).
 Helfenstein, Zeits. anorg. Chem., 23, 255 (1900).
 Hittorf, Pogg. Ann., 106, 517 (1859).
 Jahn, Grundriss der Elektrochemie, 292 (1895).
 Kahlenberg, Jour. Phys. Chem., 4, 349 (1900).
 Kohlrausch, Wied. Ann., 27, 1 (1886).
 Kohlrausch and Holborn, Leitvermögen der Elektrolyte, Leipzig (1898).
 Osmond and Houllevigne, Jour. de Phys., 7, 708 (1898).
 Ostwald, Klassiker, Nos. 81, 86, 87.
 Patterson and Guthe, Phys. Rev., 7, 257 (1898).
 Pellat and Potier, Jour. de Phys., 9, 381 (1890).
 Rayleigh and Mrs. Sidgwick, Phil. Trans., A, 175, 411 (1884).
 Richards, Collins and Heimrod, Zeits. phys. Chem., 32, 321 (1900).
 Rosa and Vinal, Bureau of Standards, Scientific Papers, No. 285 (1916).
 Shaw, B. A. Report, 411 (1886); 201 (1890).
 Skinner, B.A. Report (1900).
 Thomson, Proc. Roy. Soc., A, 53, 90 (1893); 58, 244 (1895).
 Whetham, Phil. Trans., A, 194, 321 (1900).

* A gram-equivalent is the chemical equivalent in grams of an element.

CHAPTER III.

ELECTROLYTIC CONDUCTANCE OF SOLUTIONS.

23. The electrolytic conduction process.—If an electrical potential difference is applied to an electrolytic solution, the ions within the latter will be subjected to an accelerating force according to the ordinary laws of electricity. In addition, the medium through which the ions move will exert upon them a viscous drag, or retarding force, the value of which depends upon the size of the ion, its velocity and the coefficient of viscosity of the solvent. Thus, the ion will accelerate until the two opposing forces become equal, after which it continues to travel with a steady velocity.

Consider a particle of mass m moving along the x direction under the influence of a mechanical force, X . If the velocity, u , of the particle is small, the retarding force is proportional to u and the equation of motion of the particle is

$$m \frac{du}{dt} = X - ku,$$

where k may be defined as the retarding force per unit velocity. Integrating this equation, and putting $u = 0$ at $t = 0$, we get

$$u = \frac{X}{k} \left(1 - e^{-\frac{kt}{m}} \right),$$

e being the base of Napierian logarithms. Stokes* has shown that the retarding force acting on a sphere of radius b when it moves through a fluid is $6\pi b\eta u$, where η is the coefficient of viscosity of the medium. Hence, if we assume that the particle is spherical in shape, k in the above equation is equal to $6\pi b\eta$. For water at 15°C . $\eta = 0.012$ C.G.S. units, approximately, and we may take the radius of an ion to be about 10^{-9} cm., although different ions vary in size. Thus,

$$\frac{k}{m} = \frac{6\pi b\eta}{\frac{4}{3}\pi r^3 \rho},$$

* Collected Papers, 3, 1.

where ρ is the density of the ion, so that $\frac{k}{m}$ is of the order 10^{17} , and $\left(1 - e^{-\frac{kt}{m}}\right)$ increases rapidly with t towards the limit unity. The particle, in our case the ion, rapidly attains a steady velocity given by $\frac{X}{k}$.

In an electrolytic solution containing N moles per c.c., let us assume that each mole is capable of dissociating into two gram ions, each of valency ν , and therefore each carrying equal and opposite electrical charges $\pm \nu F$. Let u_A and u_K denote the steady velocities in cms. per sec. of the anion and kation, respectively, developed under unit potential gradient, 1 volt per cm. Then, if $\frac{dE}{dx}$ is the actual potential gradient existing in the solution, each gram ion is subjected to a force $\nu F \frac{dE}{dx}$, where F is the electrical charge upon a univalent gram ion, and the steady velocities of the kations and anions are $u_K \frac{dE}{dx}$ and $u_A \frac{dE}{dx}$, respectively. If α represents the fraction of the molecules ionised, the total number of gram ions passing across a section perpendicular to the direction of flow, and of area A sq. cms., is $\alpha N A (u_K + u_A) \frac{dE}{dx}$. As each gram ion carries a charge $\pm \nu F$, and as the kations and anions move in opposite directions, the total charge passing through this section per second, *i.e.*, the current, is $\alpha N A (u_K + u_A) \frac{dE}{dx} \cdot \nu F$, due allowance being made for the fact that the opposite kinds of charges move in opposite directions. By Ohm's law the current across the section is also given by $A \sigma \frac{dE}{dx}$, where σ is the specific conductivity of the solution. Thus,

$$\sigma = \alpha N (u_K + u_A) \nu F. \quad (41)$$

In obtaining this result, we have assumed a ν -valent binary electrolyte, but equation (41) holds generally. Thus, with a solute which we may represent by $M_p X_q$, $pa = qb = \nu$, where a and b are the valencies of the radicals M and X , respectively. Hence, assuming the spontaneous ionisation hypothesis the specific conductivity of an electrolytic solution is directly proportional to the concentration of the ions, to the sum of the velocities with which they move, and to the charges which they carry.

As a rule, solutions of inorganic acids are the best conductors, followed by alkalis and salts. When increasing amounts of an electrolyte are added to water the conductivity of the resulting solution rises, attains a maximum, provided that the solubility

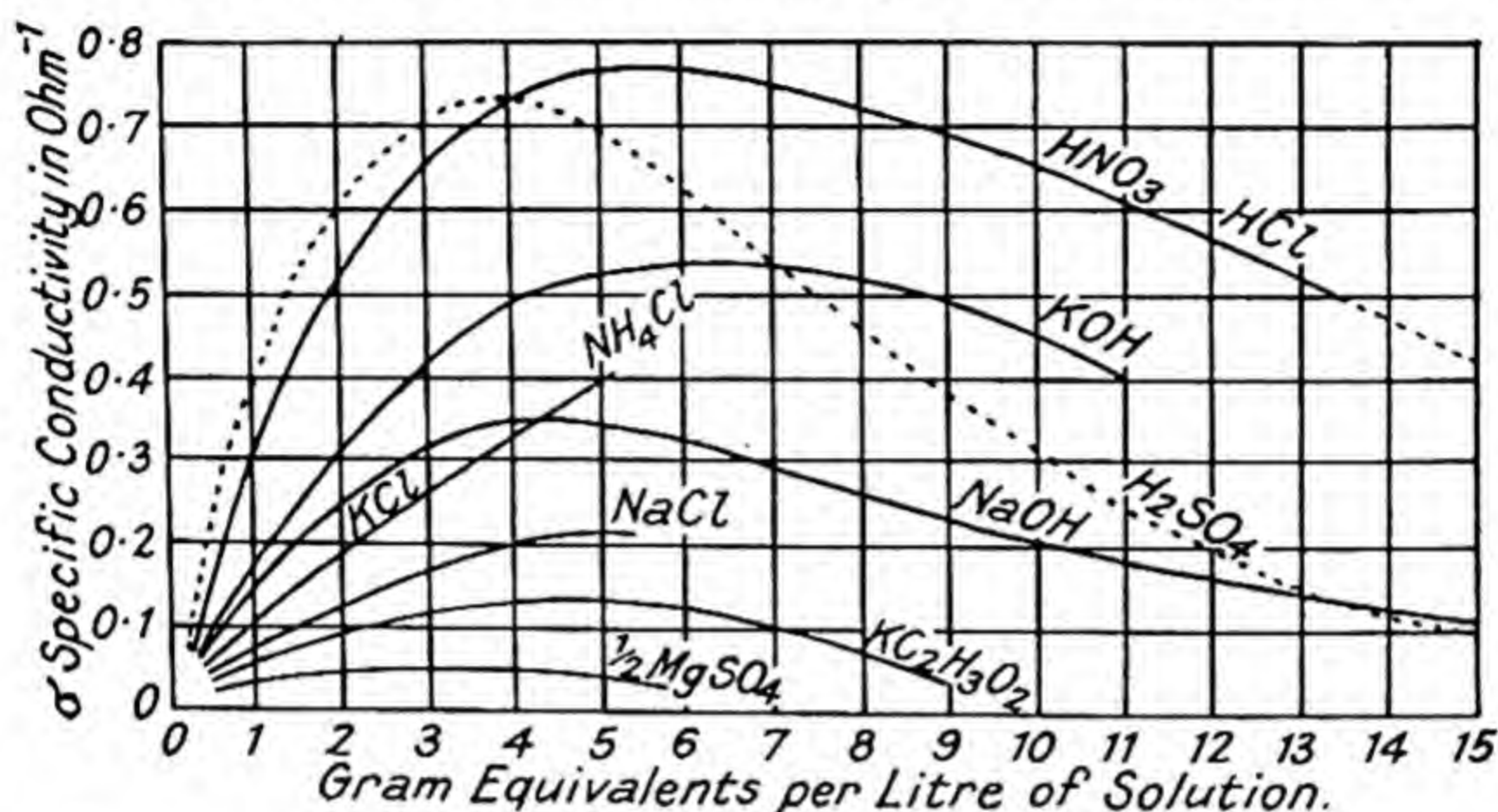


FIG. 5.—Variation of specific conductance with concentration.

of the substance permits of reaching a sufficiently high concentration, and finally decreases. The results for a few solutions are shown in Fig. 5.

24. Equivalent conductivity.—The specific conductivity divided by the concentration, in moles per c.c., of the solution is termed the *molecular conductivity*, and the specific conductivity per gram equivalent per c.c. or, as it is termed, the *equivalent conductivity*, or *equivalent conductance*, Λ , is given by

$$\Lambda = \frac{\sigma}{vN} = \alpha(u_K + u_A)F. \quad (42)$$

Its value depends only upon the ionic velocities and the degree of ionisation.

While in general the specific conductivity falls as the solution is diluted, the equivalent conductance increases, tending towards a final limit, Λ_0 , at infinitely great dilution. This is illustrated by the early measurements of Kohlrausch and Grotian* on the conductivity of aqueous sodium chloride and other solutions. Some of their results for various electrolytes are given in Fig. 6. As the measurements had to be taken over a very wide range of concentrations Kohlrausch recommended the use of diagrams in which the cube root of the concentration is taken as abscissa, and the equivalent conductance as ordinate. Curves so drawn are

* Pogg. Ann., 154, 1 (1875).

often nearly linear. In other cases it is more convenient to plot the logarithm of the concentration.

To account for the variation of equivalent conductance with concentration, let us differentiate, with respect to concentration, equation (42). We have

$$\frac{d\Lambda}{dN} = \left[\alpha \frac{d}{dN}(u_K + u_A) + (u_K + u_A) \frac{d\alpha}{dN} \right] F,$$

and since Λ increases as N decreases, $\frac{d\Lambda}{dN}$ must be negative. In other words, both or either of the expressions $\frac{d}{dN}(u_K + u_A)$, $\frac{d\alpha}{dN}$ must be negative. Hence, either the ionic velocity must depend

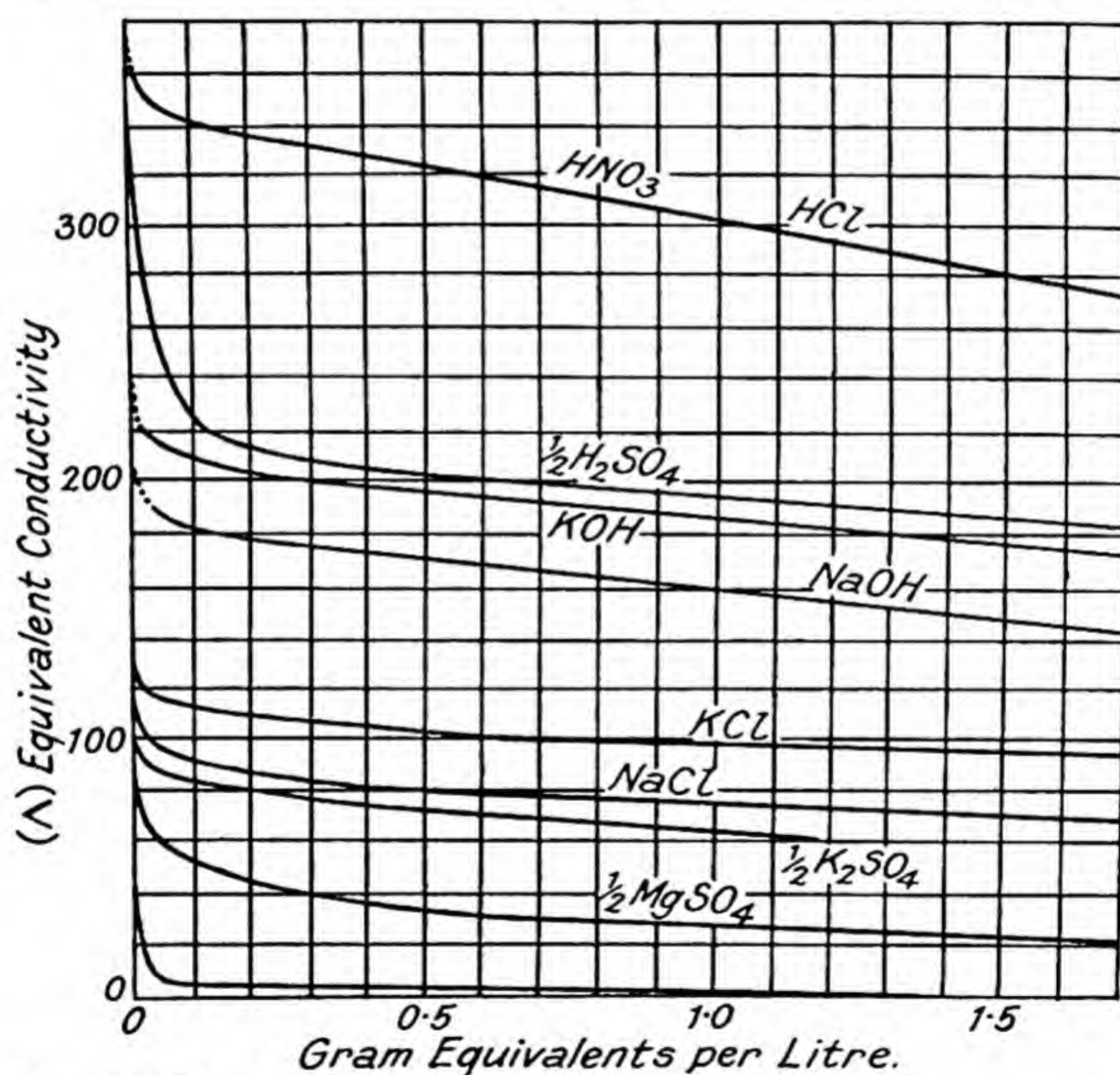


FIG. 6.—Variation of equivalent conductance with concentration.

upon the solution strength, increasing with dilution, or the degree of ionisation must increase as the solution becomes more dilute. There is certain evidence that the viscosity of the solution affects the ionic velocity, but with very dilute solutions the viscosity

must be practically that of water. Kohlrausch * has shown that for dilute electrolytic aqueous solutions the fractional rate of change of electrolytic resistance with temperature is equal to the viscosity temperature coefficient of water, and from this it has been inferred that $\frac{d}{dN}(u_K + u_A) = 0$ when $N = 0$, *i.e.*, variations in the value of Λ for dilute solutions with change in concentration are attributed primarily to changes in the coefficient $\frac{d\alpha}{dN}$. Kohlrausch † considered that the ion was not a simple sphere, but rather the centre of a group of molecules, each ion moving, as it were, in a shell of water. This idea of *hydration of the ions* has been followed up to such an extent that it is now universally accepted. The size of the shell seems to depend upon the dilution, weaker solutions giving rise to larger shells around the ions. If this is so, the effective radius of the ion increases, and its velocity decreases, with increased dilution, so that $\frac{d}{dN}(u_K + u_A) > 0$. Hence,

$\frac{d\alpha}{dN}$ must be negative, and the fraction of the molecules ionised becomes greater as the solution gets weaker. Recently, Debye and Hückel ‡ have introduced a new theory of complete ionisation in dilute solutions, the maximum concentration at which ionisation is complete depending upon the character of solvent and solute. In badly conducting aqueous solutions, the so-called *weak electrolytes*, such as phosphoric acid magnesium oxalate, *etc.*, complete ionisation is never reached; *intermediate electrolytes*, *e.g.*, iodic acid, can be regarded as completely ionised below 0.0001 normal, while electrolytes of comparatively high conductivity, the so-called *strong electrolytes*, such as the uni-univalent salts, may be considered completely ionised at much higher concentrations than this value. The theory of strong electrolytes will be discussed in greater detail later.§

When measuring the conductance of any solution, the conductivity of the solvent, particularly that of water, must be taken into account, the conductivity of water itself being due to dissolved impurities, such as ammonia, carbon dioxide, *etc.* In practice a correction factor is introduced by subtracting from the conductivity of the solution that of the water. A more accurate method of correcting for this error is given in **section (136)**.

The values of the equivalent conductance of various electro-

* *Proc. Roy. Soc., A*, 71, 338 (1903).

† *Phys. Zeits.*, 24, 185 (1923); 24, 305 (1923).

‡ *Loc. cit.*

§ See Chapter X.

lytes in water at 18° C. are given in Table II.* The concentrations are expressed in gram-equivalents per litre, a normal solution, N, containing 1 gram-equivalent per litre.†

TABLE II.

VALUES OF THE EQUIVALENT CONDUCTANCE, Λ , OF ELECTROLYTES AT 18° C.

Electrolyte.	Equivalent Conductance at Different Concentrations.						
	0.01 N.	0.02 N.	0.05 N.	0.10 N.	0.20 N.	0.50 N.	1.00 N.
NaCl	101.88	99.55	95.66	91.96	87.67	80.89	74.31
KCl	122.37	119.90	115.69	111.97	107.90	102.36	98.22
LiCl	91.97	89.75	85.97	82.28	77.80	70.60	63.27
KBr	124.31	121.78	117.69	114.14	110.32	105.30	—
KI	123.44	121.10	117.26	113.98	—	106.2	103.60
KSCN	113.87	111.51	107.67	104.21	—	95.63	91.55
NaNO ₃	98.07	95.57	91.35	87.16	82.21	73.99	65.81
KNO ₃	118.10	115.12	109.78	104.71	98.67	89.18	80.41
AgNO ₃	107.80	105.1	99.50	94.33	—	77.5	67.6
KClO ₃	111.64	108.81	103.74	99.19	93.73	85.28	—
KBrO ₃	104.7	102.0	97.3	93.0	87.8	—	—
NaIO ₃	70.86	68.56	64.43	60.46	55.45	—	—
KIO ₃	91.24	88.64	84.06	79.67	74.34	—	—
HCl	369.3	365.5	358.4	351.4	—	—	—
HNO ₃	365.0	—	353.7	346.4	—	—	—
BaCl ₂	106.67	102.53	96.04	90.78	85.18	77.29	70.14
CaCl ₂	103.37	99.38	93.29	88.19	82.79	74.92	67.54
CdCl ₂	82.2	74.2	62.1	50.1	41.0	30.4	21.4
CdI ₂	64.8	53.0	39.0	29.5	23.3	18.1	15.1
Ba(NO ₃) ₂	100.96	95.66	86.81	78.94	70.18	56.60	—
Mg(NO ₃) ₂	94.65	90.9	85.3	80.5	75.3	—	—
K ₂ SO ₄	115.8	110.3	101.9	94.9	87.7	78.4	71.6
Na ₂ SO ₄	95.7	—	83.64	77.07	69.95	—	—
Ag ₂ SO ₄	102.9	96.1	—	—	—	—	—
K ₂ C ₂ O ₄	112.83	108.07	100.77	94.79	88.57	—	73.63
H ₂ SO ₄	309.0	—	253.5	233.3	—	—	—
MgSO ₄	76.21	67.68	56.92	49.68	43.19	—	28.91
ZnSO ₄	72.9	63.8	52.8	45.4	39.1	—	26.2
CdSO ₄	70.34	60.95	49.60	42.21	35.89	28.74	23.58
CuSO ₄	71.74	62.40	51.16	43.85	37.66	—	25.77
MgC ₂ O ₄	29.6	23.0	16.4	12.7	10.0	—	—
K ₄ Fe(CN) ₆	113.4	—	93.7	84.9	77.8	—	—
Ca ₂ Fe(CN) ₆	49.9	—	38.5	35.1	32.9	—	—

25. Determination of the degree of ionisation.—

Assuming that with weak solutions $u_K + u_A$ is independent of the strength of a solution, and that for very great dilution $\alpha = 1$, we have from equation (42),

$$\alpha = \frac{\Lambda}{\Lambda_0} \quad (43)$$

* See Noyes and Falk, *Jour. Amer. Chem. Soc.*, 34, 454 (1912).

† Throughout this work conductance, or conductivity, is expressed in reciprocal ohms.

TABLE III.

DEGREE OF IONISATION OF ELECTROLYTIC AQUEOUS SOLUTIONS AT 18° C.

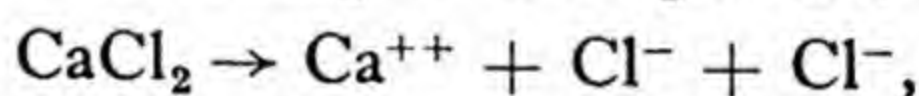
Electrolyte.			Percentage Ionisation at Different Concentrations.						
			0.005 N.	0.010 N.	0.020 N.	0.050 N.	0.100 N.	0.200 N.	0.500 N.
KCl	{ F.P.	.	96.3	94.3	91.8	88.5	86.1	83.3	80.0
	{ C.R.	.	95.6	94.1	92.2	88.9	86.0	82.7	77.9
NaCl	{ F.P.	.	95.3	93.8	92.2	89.2	87.5	85.0	82.4
	{ C.R.	.	95.3	93.6	91.6	88.2	85.2	81.8	77.3
LiCl	{ F.P.	.	94.4	93.7	92.8	91.2	90.1	—	—
	{ C.R.	.	94.9	93.2	89.0	87.8	84.6	81.2	76.6
KBr	{ F.P.	.	—	—	92.9	88.9	86.3	83.9	81.3
	{ C.R.	.	95.5	94.0	92.1	88.8	85.9	82.5	76.6
KNO ₃	{ F.P.	.	—	90.1	88.0	83.6	78.1	71.1	—
	{ C.R.	.	95.3	93.5	91.1	86.7	82.4	77.2	68.8
KIO ₃	{ F.P.	.	94.1	91.3	88.2	82.8	76.5	—	—
	{ C.R.	.	94.6	92.8	90.3	86.0	81.9	77.5	—
NaIO ₃	{ F.P.	.	93.9	91.6	89.0	84.2	77.3	—	—
	{ C.R.	.	93.9	91.7	89.0	84.2	80.1	75.2	—
HCl	{ F.P.	.	99.1	97.5	95.7	93.3	91.7	—	—
	{ C.R.	.	98.1	97.2	96.2	94.4	—	—	—
CaCl ₂	{ F.P.	.	—	—	87.6	83.7	81.5	80.4	—
	{ C.R.	.	91.0	88.2	84.9	80.2	76.4	72.7	68.8
CdI ₂	{ F.P.	.	—	59.3	54.0	40.0	22.5	10.0	—
	{ C.R.	.	67.5	57.3	46.9	—	—	—	—
Ba(NO ₃) ₂	{ F.P.	.	91.7	88.8	85.5	—	—	—	—
	{ C.R.	.	89.8	86.1	81.8	74.4	67.9	60.9	50.4
K ₂ SO ₄	{ F.P.	.	92.9	89.9	85.7	78.5	73.0	66.7	56.8
	{ C.R.	.	90.5	87.2	83.2	77.1	72.2	67.3	61.8
Na ₂ SO ₄	{ F.P.	.	—	—	86.7	79.5	73.6	67.2	56.7
	{ C.R.	.	89.3	85.7	—	75.6	70.4	65.2	—
MgSO ₄	{ F.P.	.	69.4	61.8	53.6	42.0	32.4	22.3	8.4
	{ C.R.	.	74.0	66.9	59.6	50.6	44.9	40.3	—
CuSO ₄	{ F.P.	.	61.6	54.5	45.5	31.8	—	—	—
	{ C.R.	.	70.9	62.9	55.0	45.5	39.6	35.1	—
ZnSO ₄	{ F.P.	.	66.5	58.2	48.9	—	—	—	—
	{ C.R.	.	71.0	63.3	55.6	46.4	40.5	36.0	—
K ₃ Fe(CN) ₆	{ F.P.	.	89.4	86.8	77.8	—	—	—	—
	{ C.R.	.	86.9	82.7	—	—	—	—	—

It will be observed that the degree of ionisation of salts of the same type, such as, for example, salts composed of univalent radicals, is approximately the same at the same concentration, and this is particularly true at the lower concentrations, where the divergence in many cases is scarcely greater than the experimental error. The strong acids and bases, however, have a markedly higher ionisation than the salts, and salts of higher types exhibit a lower degree of ionisation than simple salts.

The two methods of calculating α give values which, for most uni-univalent substances, agree with each other within 2 per

cent. up to concentrations of 0.1 N, and the same remark applies to uni-bivalent salts, K_2SO_4 , $Pb(NO_3)_2$, even up to 0.2 N. The halides and sulphates of bivalent metals, and also lithium chloride and sodium sulphate, on the other hand, show, as a rule, much larger deviations at concentrations of 0.1 N and 0.2 N.

It must be remembered that the calculation of α from freezing-point depressions is based upon the principle that the ions and ionised molecules behave like the molecules of organic substances, while the calculation from conductance measurements assumes that the velocity of the ions is independent of their concentration, except in so far as the latter affects the viscosity of the solution. In addition, both methods involve the assumption that the only forms in which the substance exists in solution are the ultimate simple ions into which the molecules dissociate at great dilution, and the un-ionised molecules themselves. This last assumption is certainly fulfilled in the case of most uni-univalent electrolytes, but with salts of higher type there is always a possibility that the ionisation process, assumed in calculating the ionisation from the conductivity measurements, does not correspond to the true reaction. Thus, in determining α for $CaCl_2$, it is assumed that the reaction takes place according to the equation,



whereas intermediate ions, such as $CaCl^+$, may be formed thus,



in which case it is impossible to calculate the degree of ionisation from conductivity measurements. Noyes and Eastman * have established the existence of intermediate ions in sulphuric acid solutions, and Harkins † has shown that intermediate ions are present in solutions of many salts of higher type.

The molecular weights, as determined by methods involving osmotic pressure effects, may be expected to be in error, since the laws of dilute solutions are assumed in calculating their values, and it is fairly certain that these laws do not apply. There is the possibility that where actual agreement exists between the values of α , determined by the two methods, it arises from corresponding inaccuracies in the two methods, or from a compensation of errors. Noyes and Falk ‡ point out that the agreement really does arise from such compensation, as is evident from the fact that the ionisation values, derived from the conductance ratio, decrease with concentration far more slowly than expected.

* Carnegie Reports, No. 19, 241.
† *Jour. Amer. Chem. Soc.*, 33, 1808 (1911).

‡ *Loc. cit.*

26. Independent migration of the ions.—Consider a simple case of conductance where the ions are deposited on the electrodes. From equation (41), $\frac{u_K}{u_K + u_A}$ will be the fraction of the charge carried by the kations, and $\frac{u_A}{u_K + u_A}$ that conveyed by the anions. These ratios, which Hittorf* termed *transference numbers* of the kation and anion, respectively, may be denoted by the symbols n_K and $(1 - n_K)$. Hence, putting $U = \alpha F u_K$ and $V = \alpha F u_A$ we have from equation (42),

$$\left. \begin{aligned} \Lambda &= U + V, \\ U &= n_K \Lambda, \\ V &= (1 - n_K) \Lambda \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (47)$$

These relations express *Kohlrausch's law* † of the independent migration of the ions which states that, in a solution of a single electrolyte the two ions move independently of each other, in other words, the equivalent conductance of a binary electrolyte is equal to the sum of the conductances of the two ions, U and V being termed the *equivalent conductances of the kation and anion*, respectively. The rules expressed in equations (47) hold good for those electrolytes which are completely dissociated, but they likewise apply to the comparison of electrolytes existing in the same state of dissociation. When Kohlrausch developed his law, the difference between the free ions and the inactive molecules of an electrolyte was not recognised, but on verifying the law from his conductance measurements, the calculated values of the transference numbers were in good agreement with those determined by Hittorf in all cases where the electrolytes were in the same degree of dissociation, otherwise there were decided deviations. By measuring the equivalent conductance and transference numbers of dilute silver salts, Kohlrausch ‡ showed that the relation between these quantities was strictly accurate when the two values refer to completely dissociated electrolytes. Kohlrausch's law demands that the equivalent conductance at infinite dilution of the potassium ion, for example, should have the same value whether derived from chlorides, nitrates, *etc.*, and relations similar to the following should hold :—

$$\Lambda_0(\text{KCl}) - \Lambda_0(\text{NaCl}) = \Lambda_0(\text{KNO}_3) - \Lambda_0(\text{NaNO}_3),$$

* Pogg. Ann., 89, 177 (1853).

† Gottinger Nachrichten, 213 (1876).

‡ Zeits. Elektrochem., 13, 333 (1907).

or, more generally,

$$\Lambda_0(\text{MX}) - \Lambda_0(\text{M}'\text{X}) = U_0 - U_0'. \quad (48)$$

Ferguson and Vogel * have examined this law of the independent migration of the ions, and compared their results with those obtained from the values of Λ_0 as measured by Kohlrausch. The comparative results for 18° C. are shown in Table IV.

TABLE IV.
INDEPENDENT MIGRATION OF THE IONS.

Electrolytes.	Values of $\Lambda_0[\text{MX}] - \Lambda_0[\text{MX}']$ and $\Lambda_0[\text{MX}] - \Lambda_0[\text{M}'\text{X}]$.	
	Ferguson and Vogel.	Kohlrausch.
NaCl—NaNO ₃ . . .	3.54	3.66
KCl—KNO ₃ . . .	3.65	3.60
LiCl—LiNO ₃ . . .	3.67	3.70
KCl—NaCl . . .	21.02	21.11
KNO ₃ —NaNO ₃ . . .	20.91	21.17
KIO ₃ —NaIO ₃ . . .	21.00	21.07
KCl—LiCl . . .	30.97	31.22
KNO ₃ —LiNO ₃ . . .	30.99	31.32
KIO ₃ —LiIO ₃ . . .	31.01	31.13
NaCl—NaIO ₃ . . .	31.48	31.57
KCl—KIO ₃ . . .	31.50	31.61
LiCl—LiIO ₃ . . .	31.54	31.52

27. Conductance, or mobility, of the ions.—Since the value of the equivalent conductance, Λ , is given by

$$\Lambda = U + V,$$

it is evident that if we know Λ , and the value of the transference number, n_K , where

$$n_K = \frac{U}{U + V},$$

we may determine the value of U , the equivalent conductance, or *mobility* as it is often called, of the kation. Subtracting the result from the value of Λ gives the mobility of the anion. Thus the equivalent conductance of potassium chloride in aqueous solution at infinite dilution is 130.14,† the chloride transference number ‡

* *Phil. Mag.*, 50, 983 (1925).

† See Ferguson and Vogel, *loc. cit.*

‡ See Noyes and Falk, *Jour. Amer. Chem. Soc.*, 33, 1436 (1911).

under the same conditions being 0.5040. The mobility of the Cl^- ion is therefore 65.54, and that of the potassium ion, 64.60. All these numbers refer to 18°C . Having determined, accurately, the potassium ion mobility, and knowing the values of Λ_0 for different electrolytic solutions, we may proceed to calculate the mobilities of other ions by utilising the law of independent ionic migration, *e.g.*, the value of Λ_0 for potassium sulphate is 132.85,* and therefore the mobility of the $\frac{1}{2}\text{SO}_4^{--}$ ion is

$$132.85 - 64.60 = 68.25.†$$

Assuming that the conductance of the chloride ion remains the same in all equi-concentrated aqueous solutions, at the same temperature, it is evident that in hydrochloric acid, potassium chloride and sodium chloride solutions the anion carries the same current, and therefore the difference in the conducting powers of these electrolytes must be due to the difference in the conducting powers of the kations. The mobility of the hydrogen ion, although an important constant, has not yet been determined with any great degree of accuracy. Using the accurate results of Kraus and Parker ‡ for iodic acid and those of Parker § for hydrochloric acid, Ferguson and Vogel || calculated $\Lambda_0 = 425.68$ for hydrochloric acid and $\Lambda_0 = 389.54$ for iodic acid, both measured at 25°C . As there are no accurate measurements of the conductivity of aqueous iodate solutions at 25°C ., Ferguson and Vogel subtracted the value of the mobility at infinite dilution of the chloride ion—76.63—from the value of Λ_0 for hydrochloric acid—425.68—and obtained the value 349.05 for the hydrogen ion mobility at 25°C . From this result they find that the mobility of the iodate ion, at infinite dilution and 25°C ., is 40.49. The values of the equivalent conductances at infinite dilution of various ions, as calculated by Ferguson and Vogel, ¶ are given in Table V., together with those determined by Kohlrausch.**

The hydrogen and hydroxyl ions are distinguished from the others by their high mobility values. This fact is in agreement with the comparatively great conductivity values shown by solutions of strong acids and bases. The mobilities of the different ions appear to bear no simple relation to the ionic constitution. Thus lithium, which is lighter, and has a smaller atomic volume than the remaining alkali metals, has the smallest mobility.

* See Ferguson and Vogel, *loc. cit.*

† See Noyes and Falk, *Jour. Amer. Chem. Soc.* **33**, 1436 (1911).

‡ *Jour. Amer. Chem. Soc.*, **44**, 2429 (1922); **45**, 2029 (1923).

§ *Ibid.*, **45**, 2017 (1923).

|| *Loc. cit.*

¶ *Phil. Mag.*, **4**, 233 (1927).

** *Zeits. Elektrochem.*, **8**, 288, 626 (1902); **14**, 129 (1908).

TABLE V.

IONIC EQUIVALENT CONDUCTANCE AT INFINITE DILUTION.

Kation.	Ionic Equivalent Conductance (U_0).				Anion.	Ionic Equivalent Conductance (V_0).			
	(Ferguson and Vogel.)			(Kohl- rausch.)		(Ferguson and Vogel.)			(Kohl- rausch.)
	0° C.	18° C.	25° C.	18° C.		0° C.	18° C.	25° C.	18° C.
K ⁺	40.3	64.60	75.63	64.67	Cl ⁻	41.2	65.54	76.63	65.44
Na ⁺	25.5	43.48	51.42	43.55	NO ₃ ⁻	39.5	61.83	—	—
Li ⁺	17.8	33.53	—	33.44	IO ₃ ⁻	20.3	34.00	—	33.87
Tl ⁺	43.5	65.53	—	66.00	Br ⁻	—	67.70	77.85	67.63
Cs ⁺	—	67.53	—	68.2	I ⁻	—	66.06	—	66.40
Ag ⁺	—	54.36	—	54.02	F ⁻	—	46.77	—	46.64
$\frac{1}{2}$ Ca ⁺⁺	—	52.19	—	—	CNS ⁻	—	56.48	—	56.63
$\frac{1}{2}$ Sr ⁺⁺	—	51.66	—	—	ClO ₃ ⁻	—	54.97	—	55.03
$\frac{1}{2}$ Ba ⁺⁺	—	55.04	—	56.3	$\frac{1}{2}$ SO ₄ ⁻	—	68.25	—	—
$\frac{1}{2}$ Pb ⁺⁺	—	61.61	—	61.5	$\frac{1}{2}$ C ₂ O ₄ ⁻	—	61.13	—	—
$\frac{1}{2}$ Mg ⁺⁺	—	45.78	—	46.0	ClO ₄ ⁻	36.5	54.80	—	—
$\frac{1}{2}$ Cd ⁺⁺	—	46.45	—	—	CH ₃ COO ⁻	—	32.48	—	35.0
$\frac{1}{2}$ Cu ⁺⁺	—	45.91	—	—	Picrate	14.7	25.14	—	—
$\frac{1}{2}$ Zn ⁺⁺	—	46.01	—	45.6	MnO ₄ ⁻	—	—	61.19	—
H ⁺	—	—	349.05	318	OH ⁻	—	175.4	—	174

As the strength of the solution increases the ionic mobility is lowered. Ferguson and Vogel* suggested that the relation between these variables might be represented by the equation,

$$U_0 = U + bC^d,$$

where U is the mobility at a solution concentration C , U_0 , that at infinite dilution and b and d are constants.

The equivalent conductance of infinitely dilute solutions may be calculated from the constituent ionic mobilities. Thus, while it is comparatively easy to measure, or rather extrapolate, the equivalent conductance at great dilution of potassium chloride, this is not the case with ammonia. However, since,

$$\Lambda_0(\text{NH}_4\text{OH}) = U_0(\text{NH}_4^+) + V_0(\text{OH}^-),$$

then at 18° C.,

$$\Lambda_0(\text{NH}_4\text{OH}) = 64.7 + 175.4 = 240.1,$$

and thus Λ_0 is determined. This method may be applied to all electrolytes.

28. Ionic mobility and temperature.—The ionic mobilities increase about 1.5 to 2.7 per cent. per degree C. rise of tempera-

* *Phil. Mag.*, 4, 240 (1927).

ture, the temperature coefficient decreasing as the mobility increases, so that the differences between the mobilities of different ions tend to diminish as the temperature rises. Kohlrausch * has shown that the relation between the mobility, U , of an ion and its temperature coefficient, a , where $a = \frac{1}{U} \frac{dU}{dT}$, may be represented by the equation,

$$a = 0.0136 + \frac{0.67}{18.5 + U}.$$

Other formulæ proposed include,

$$a = \frac{0.0348}{\log U + 0.207},$$

and

$$a = 0.0134 + 0.64 \cdot \frac{1}{U} - 6.94 \cdot \frac{1}{U^2}.$$

No theoretical interpretation has been given to these formulæ, but in spite of their different forms they lead to results which agree well with observations. The values of a , as determined by Kohlrausch for various ions, are given in Table VI.

TABLE VI.

TEMPERATURE COEFFICIENTS OF IONIC CONDUCTANCES AT 18° C.

Ion.	Value of a .	Ion.	Value of a .	Ion.	Value of a .
Li ⁺	0.0265	Cs ⁺	0.0212	OH ⁻	0.0180
Na ⁺	0.0244	Rb ⁺	0.0214	NO ₃ ⁻	0.0295
Ag ⁺	0.0229	Cl ⁻	0.0216	CH ₃ COO ⁻	0.0238
K ⁺	0.0217	I ⁻	0.0213	$\frac{1}{2}$ Zn ⁺⁺	0.0251
H ⁺	0.0153	CNS ⁻	0.0221	$\frac{1}{2}$ Mg ⁺⁺	0.0256
NH ₄ ⁺	0.0222	IO ₃ ⁻	0.0234	$\frac{1}{2}$ Ba ⁺⁺	0.0238

29. Law of mass action applied to electrolytes.—The hypothesis of Arrhenius, that electrolytes dissolved in water are more or less dissociated into ions, is supported, as we have seen, by conductance and freezing-point measurements. Molecules are dissociated and the resulting ions then recombine in different ways. But dissociation is a kinetic phenomenon. It is not that some molecules are always dissociated and others not, but that each molecule is broken up, from time to time, by some especially violent collision with its neighbours, and again, that detached ions

* *Loc. cit.*

frequently recombine. In this manner a certain average state of dissociation is maintained with considerable uniformity, but any individual ion may combine, and then return to the ionic form, many times a second. The state of equilibrium that exists at any time is of the statistical character familiar in the theory of gases, *i.e.*, a certain average proportion of the molecules are dissociated, but no particular molecules are always in this state. If we assume a simple, but at the same time the most important, case of dissociation of a binary electrolyte, which may be represented by



there will be, neglecting the solvent effect, three sets of constituents, M^+ ions, X^- ions and undissociated molecules, MX . If C is the total concentration of the electrolyte, the concentration of each set of ions will be αC , and that of the undissociated molecules, $(1 - \alpha)C$. Hence, applying the mass action law, equation (30),

$$\frac{\alpha C \cdot \alpha C}{(1 - \alpha)C} = K,$$

or

$$\frac{C\alpha^2}{1 - \alpha} = K, \quad . \quad . \quad . \quad . \quad (49)$$

where K is a function of the temperature only, and is termed the *equilibrium constant* for the electrolyte in question.

This relationship, which is known as *Ostwald's dilution law*,* only holds if the solution is so dilute that the laws of dilute solutions apply to it. As the concentration is raised, a value is reached at which these laws fail, and K becomes a function both of the concentration and of the temperature. Substituting $\alpha = \frac{\Lambda}{\Lambda_0}$ we

have
$$\frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)} = K, \quad . \quad . \quad . \quad . \quad (50)$$

which gives a relationship between the concentration and the equivalent conductance of a binary electrolyte. The value of Λ_0 is determined by some extrapolation method, after which the constancy of K may be tested by substituting in equation (50) corresponding values of C and Λ . Table VII. shows some results calculated by Kendall.†

For acetic acid K is constant and independent of concentration; but for cyanoacetic acid the value of K falls steadily with increasing dilution, and only approaches a limit in very weak solutions.

* *Zeits. phys. Chem.*, 2, 270 (1888).

† *Jour. Chem. Soc.*, 101, 1283 (1912).

TABLE VII.

VARIATION OF THE EQUILIBRIUM CONSTANT WITH CONCENTRATION.

Acetic Acid.				Cyanoacetic Acid.			
Litres per Gram- Equiva- lent.	Values of			Litres per Gram- Equiva- lent.	Values of		
	Λ_0 .	100α .	$100K$.		Λ_0 .	100α .	$100K$.
13.57	6.086	1.570	0.001845	16.82	88.0	22.80	0.400
27.14	8.591	2.216	0.001851	33.64	117.0	30.31	0.392
54.28	12.09	3.118	0.001849	67.28	152.5	39.50	0.383
108.56	16.98	4.380	0.001849	134.56	193.9	50.23	0.378
217.1	23.81	6.141	0.001851	269.1	238.7	61.84	0.372
434.2	33.22	8.568	0.001849	538.2	282.6	73.20	0.372
868.4	46.13	11.90	0.001850	1076.4	320.0	82.89	0.373
1,737.0	63.60	16.41	0.001854	2153.0	347.1	89.90	0.373
3,474.0	86.71	22.36	0.001855	4306.0	364.8	94.52	0.378
6,948.0	116.8	30.13	0.001870	∞	386.0	—	—
∞	387.7	—	—				

This acid belongs, therefore, to a class of transition acids which follow the dilution law only in very weak solutions. Ostwald * confirmed the law for 250 acids, and Bredig † for 50 bases. Wegscheider, ‡ working with various solutions, found that the equilibrium constant, K , decreased in value as the solution strength increased, and he attributed this to the increase in the viscosity of the solution with concentration. In general, the variation in the values of K becomes appreciable for the majority of organic acids at concentrations within the range 16-32 litres per mole.

For strong electrolytes the equilibrium "constant," or dissociation constant as it is sometimes called, is by no means constant, and Ostwald's dilution law is not in accordance with the observed change of equivalent conductance with concentration. We find, for instance, that with high valence salts, such as $K_4Fe(CN)_6$ and $La_2(SO_4)_3$, the value of K varies approximately a million-fold within the concentration range 10^{-5} — 1 mole per litre. As an illustration of this variation, we may take the case of two typically strong electrolytes, potassium and sodium chlorides, for which the values of K at different concentrations are as follows § :—

* *Zeits. phys. Chem.*, 2, 270 (1888) ; 3, 170, 241, 369 (1889).

† *Ibid.*, 13, 289 (1894).

‡ *Ibid.*, 69, 603 (1909).

§ The values of Λ_0 are taken from the data of Ferguson and Vogel (*loc. cit.*) and those of Λ from Noyes and Falk's data (*loc. cit.*).

KCl, $\Lambda_0 = 130.04$		NaCl, $\Lambda_0 = 109.02$.	
Concentration.	Values of K .	Concentration.	Values of K .
0.0001N	0.0124	0.0001N	0.0108
0.001N	0.0450	0.001N	0.0399
0.01N	0.150	0.01N	0.133
0.1N	0.534	0.1N	0.483
1N	2.332	1N	1.54

It is evident from these results that the values of K depend to a great extent upon the concentration at which they are measured. Weiland * has shown, however, that the equilibrium constant for potassium chloride approaches a constant value as its solution becomes sufficiently dilute, the limiting value at zero concentration being 0.020 ± 0.001 , but this value depends very much upon the value chosen for the equivalent conductance at infinite dilution, a small error in this value creating a large percentage error in the resulting value of K .

Washburn † found that in sufficiently dilute solutions, *i.e.*, for most practical purposes below $C = 0.0001N$, all uni-univalent salts of strong acids and bases obey the mass action law, and all of them have the same degree of ionisation. Also, in the case of two salts, such as potassium chloride and bromide, which resemble each other very closely, the values of the ionisation fractions and equilibrium constants are identical below $0.005N$. These results have been criticised by Gross and Redlich,‡ who point out that the value of $\frac{dK}{dC}$ is equal to zero only when $C = 0$, and that actual measurements have not yet been made over a range of dilutions which give a constant value for K .

Kraus and Parker's experiments § with iodic acid, and Parker's experiments || with hydrochloric acid are often quoted as affording evidence for the validity of the mass-action law at low concentrations. For iodic acid at $25^\circ C$. the value of K is constant over a fairly wide range ($C = 0.00005$ to $C = 0.001$ normal), but the constancy of K for hydrochloric acid over a range depends upon the value of Λ_0 adopted for this acid.¶

To account for these discrepancies we must assume that the equivalent conductance Λ , because of some variation in the ionic mobility, does not measure the ionic concentration. On the other hand, the substance in solution may not obey the ideal gas laws which are assumed to hold for dilute solutions.

* *Jour. Amer. Chem. Soc.*, **40**, 106 (1918).

† See paper under note *.

‡ *Zeits. phys. Chem.*, **104**, 315 (1923).

§ *Jour. Amer. Chem. Soc.*, **44**, 2429 (1922).

|| *Ibid.*, **45**, 2017 (1923).

¶ See Ferguson and Vogel, *Phil. Mag.*, **4**, 4 (1927).

Arrhenius * concluded, from experiments on the inversion rate of sucrose by weak acids, that the equilibrium constants of these acids, and of weak electrolytes in general, were greatly enhanced by the mere presence of strong electrolytes. For instance, he found that even so dilute a solution as 0.125N of potassium chloride apparently increased the hydrogen ion concentration of a 0.025N acetic acid solution by 12.6 per cent. McBain and Coleman † have shown, however, that when more accurate data for the degrees of ionisation are used this is not the case.

30. Strong electrolytes.—The anomalous behaviour of strong electrolytes cannot be accounted for satisfactorily by the mass action law, and attempts to explain their behaviour have been made by considering them as practically completely ionised, the electric forces between the ions being responsible for the observed anomalies. The theory of complete ionisation postulates that the diminution in the equivalent conductance of electrolytic solutions, as the concentration increases, is due to a change in the mobility of a fixed number of ions instead of to a change in the number having a fixed mobility. On this hypothesis Debye and Huckel ‡ showed that, as a result of the electrical attraction between oppositely charged ions, there is, in the immediate neighbourhood of any single ion, an excess of ions bearing opposite charge, and owing to the finite time which is necessary for the re-distribution of the ions to occur around an ion that is in motion through the solution, there will always be an excess number of ions of opposite sign in its rear. Thus, the ion will be subjected to a retardation when moving in an electric field. Further, as the ions of opposite sign are moving in opposite directions, and as both sets of ions are supposed to drag with them a certain amount of solvent, viscous resistance to the motion of the ion will be greater than if the solvent were simply at rest. Both of these effects act in such a way as to reduce the speed of the ions, and both will increase in magnitude as the concentration of the solution increases. The effects will depend both upon the valency of the ions and the specific inductive capacity of the solvent.

Many investigators from different points of view have suggested that the ionisation of strong electrolytes was much greater than appeared to be the case from the usual calculations on the basis of conductivity data. Milner § attempted to calculate, quantitatively, the effect of the ionic forces on the thermodynamic

* *Zeits. phys. Chem.*, **31**, 197 (1899).

† *Jour. Chem. Soc.*, **105**, 1517 (1914); **115**, 1332 (1919).

‡ *Phys. Zeits.*, **24**, 305 (1923).

§ *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913).

functions of a salt solution, and although mathematical difficulties impeded a strict solution of the problem, the approximate results showed a surprisingly good agreement with the experimental data, and strongly favoured the theory of complete ionisation. The theory is subject to the limitation that the formulæ deduced from it are only valid at high dilutions, approximately below 0.1N, since a 0.1N solution is too concentrated to be exempt from errors. It has, however, the merit of leading to a relation between conductivity and concentration which fits the data for strong electrolytes, such as sodium chloride, just as well as Ostwald's law fits the data for weak electrolytes, such as acetic acid.

Debye and Huckel provided a theoretical basis for the relationship,

$$\Lambda_0 - \Lambda_c = k\sqrt{C},$$

where Λ_c is the equivalent conductance at a concentration C and k is a constant, which Kohlrausch had deduced experimentally as a general expression for the effect of changes of concentration upon the equivalent conductance of an electrolyte. Although there are many electrolytes to which the theory of complete ionisation does not apply, the experimental verifications with strong electrolytes are so numerous that the theory is widely accepted. A more complete account of this complete ionisation theory is given in **Chapter X**.

31. Conductivity of non-aqueous solutions.—So far, we have considered the conductance in aqueous solutions, but the property of forming conducting solutions is one not restricted entirely to the solutions formed by dissolving electrolytes in water. The peculiar properties of water as a solvent have hitherto focussed practically all the attention to this substance, and solutions of electrolytes in non-aqueous solvents have been characterised to some extent by a lack of co-ordination and of accuracy. In attempting to account for the properties of electrolytic aqueous solutions, those properties of the solutions which are characteristic of aqueous solutions alone, must be distinguished from those which are characteristic of electrolytic solutions in general, a task which is by no means simple. Lately, however, very accurate measurements are being made with non-aqueous solvents which must inevitably lead to a better understanding of the conduction process.

32. Conductivity of salts in alcohols.—The alcohols, from a constitutional point of view, are very closely related to water, more so in fact than any other solvent, and they may be considered

as water in which one of the hydrogen atoms has been substituted by a hydrocarbon group. In general, the ionising power of the alcohols decreases as the complexity of the carbon group increases, and therefore we should expect methyl alcohol to be the one most closely resembling water. Frazer and Hartley * have made very accurate measurements of the electrical conductivity at concentrations ranging from 0.0001N to 0.002N of fifteen uni-univalent salts in methyl alcohol. Some of their results are given in Table VIII. :—

TABLE VIII.

EQUIVALENT CONDUCTANCE OF SALTS IN METHYL ALCOHOL AT 25° C.

Salt.	Concentration in Gm. Eq. per Litre $\times 10^4$.	Λ_c .	Λ_0 .	Salt.	Concentration in Moles per Litre $\times 10^4$.	Λ_c .	Λ_0 .
LiCl	2.7370 6.5055 17.9420	87.24 85.16 81.42	90.90	KNO ₃	1.8169 4.8517 9.6292	109.97 107.06 103.94	114.55
NaCl	2.7933 7.2393 18.7080	93.19 90.76 87.04	96.95	RbNO ₃	3.4020 7.2403 13.5100	111.57 108.61 105.06	118.15
KCl	3.1766 8.0981 20.397	100.41 97.62 93.33	105.05	CsNO ₃	0.6104 2.9550 5.9400	120.26 116.36 113.70	122.95
RbCl	3.8715 7.9862 17.0090	103.11 100.60 97.10	108.65	AgNO ₃	3.4820 9.6510 16.1670	104.53 99.01 94.85	112.95
CsCl	4.6383 9.0880 15.0370	107.32 104.82 102.26	113.60	KBr	5.0406 10.6330 18.3780	103.48 100.83 98.25	109.35
LiNO ₃	4.7910 9.7383 14.8170	94.65 92.32 90.57	100.25	KI	2.5020 8.0458 13.8724	110.73 107.45 105.16	114.85
NaNO ₃	5.9790 12.0660 17.3940	99.44 96.41 94.45	106.45	NaBr HCl NH ₄ Cl NaOCH ₃ NaClO ₄			101.5 193.5 111.00 98.40 115.10
KF			94.0				

If the values of the equivalent conductance, Λ_c , are plotted against the square root of the equivalent concentration, and the graphs compared with those for aqueous solutions, it is found that the slopes of the lines are about four times as steep for methyl alcohol

* *Proc. Roy. Soc., A*, 109, 351 (1925).

as for water; and whereas with water they are approximately parallel for the salts examined, with methyl alcohol there are more definite differences in slope. Frazer and Hartley found that with the chlorides and nitrates of the alkali metals there was an increase in the slope in passing from lithium to caesium, and, as a group, the nitrates have a steeper slope than the chlorides. The slope of the lines in methyl alcohol evidently depends upon both the ions present, and the contrast between the behaviour in water, and in this solvent, shows that the individual differences between various electrolytes are much more marked in non-aqueous solvents than in water, in which the properties of electrolytes seem to depend more exclusively upon the valence types of the constituent ions.

These experimenters also confirmed Kohlrausch's law of the independent mobility of the ions at infinite dilution in methyl alcohol. Thus, they found that for the alkali metals, the differences in the equivalent conductances at infinite dilution of the nitrates and chlorides at 25° C. were as follows:—

	Li.	Na.	K.	Rb.	Cs.
Λ_0 (nitrate) - Λ_0 (chloride)	9.35	9.50	9.50	9.50	9.35

and therefore it is possible to determine the individual values of the mobilities once the values of Λ_0 and of the transport numbers of any one of the salts concerned have been obtained. The values of the mobilities of different ions in infinitely dilute solutions of methyl alcohol are shown in Table IX., and for the sake of com-

TABLE IX.

IONIC MOBILITIES IN METHYL ALCOHOL AND IN WATER AT 25° C.

Ion.	Value of U_0 in Methyl Alcohol. (A)	Value of U_0 in Water. (B).	Ratio $\frac{A}{B}$.	Ion.	Value of V_0 in Methyl Alcohol. (A).	Value of V_0 in Water. (B).	Ratio $\frac{A}{B}$.
Li	39.6	39.6	1.00	F ⁻	40.2	54.4	0.74
Na ⁺	45.7	50.9	0.90	Cl ⁻	51.3	75.4	0.68
K ⁺	53.8	74.4	0.72	Br ⁻	55.5	77.5	0.71
Rb ⁺	57.4	77.6	0.74	I ⁻	61.0	76.0	0.81
Cs ⁺	62.3	78.1	0.80	—	—	—	—
Ag ⁺	52.2	63.0	0.83	NO ₃ ⁻	60.8	70.8	0.85
NH ₄ ⁺	59.8	73.9	0.81	ClO ₄ ⁻	69.4	76 ?	0.90
H ⁺	142.2	349	0.41	OMe	52.7	196(OH)	—

parison the mobilities in water are also given. The ratio of the mobilities in the two solvents varies from ion to ion, and there is no simple relation between them. The relative speeds of the

ions in methyl alcohol are smaller than would be expected from its low viscosity coefficient, but this may be due to the formation of larger complexes in the alcohol than in water.

It is interesting to note that in methyl alcohol, as in water, the mobilities of the alkali metal ions increase with rising atomic number and atomic volume. In the case of the halogens the mobilities in methyl alcohol increase regularly with atomic number, but in water the chloride, bromide and iodide ions have prac-

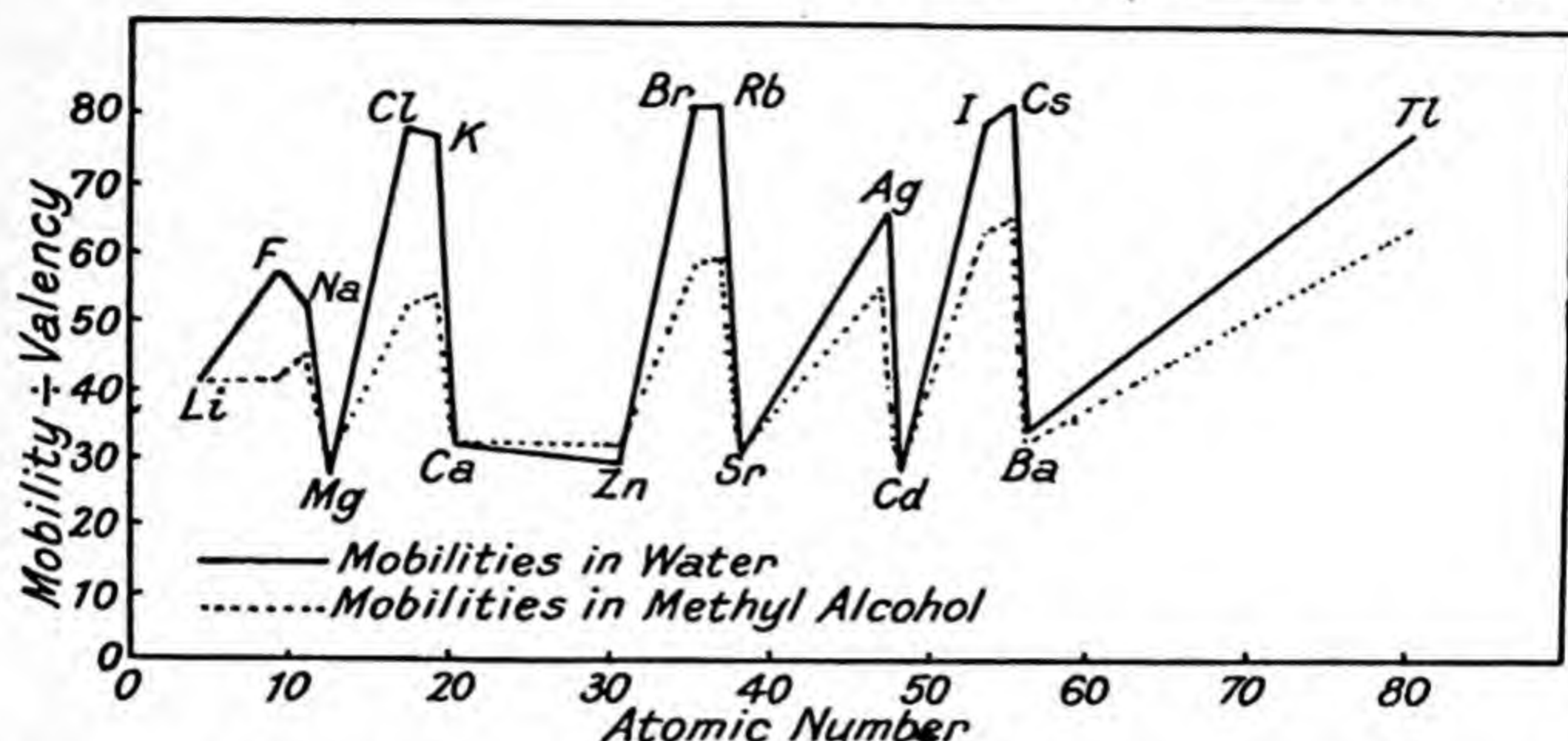


FIG. 7.—Mobility of ions in methyl alcohol and in water. (Frazer and Hartley.)

tically the same mobility. These facts are illustrated in Fig. 7, which is taken from Frazer and Hartley's paper.

Kraus and Bishop* measured the molecular conductance, Λ , of anhydrous calcium nitrate, and of magnesium nitrate hexahydrate, in anhydrous propyl alcohol at 18° C. Their results are given in Table X., where C is the concentration expressed in millimoles per litre.

TABLE X.

EQUIVALENT CONDUCTANCE OF ANHYDROUS PROPYL ALCOHOL SOLUTIONS.

Anhydrous Calcium Nitrate.							
$C \times 10^3$	0.363	0.792	1.617	5.908	14.320	24.930	43.290
Λ	5.140	3.834	2.894	1.798	1.258	0.976	0.722
Magnesium Nitrate Hexahydrate.							
$C \times 10^6$	394	865	1,942	6,406	9,804	19,890	—
Λ	12.422	10.730	8.932	6.408	6.026	4.674	—

* *Jour. Amer. Chem. Soc.*, 43, 1568 (1921).

33. Conductivity of liquid ammonia solutions at -33°C .

—Liquid ammonia possesses strong ionising power, and the conductivity of many substances in this solvent has been measured by Franklin and Kraus.* Acid amides conduct, but while some are poor conductors, others approach the uni-univalent aqueous salt solutions in their conductivity. Many nitro compounds give solutions which are excellent conductors. Potassium cyanide behaves normally in ammonia solutions, but the cyanides of the heavy metals exhibit unique behaviour. In the first place, the conductivity is low, but more striking is the fact that the molecular conductivity, instead of increasing rapidly with dilution, at first decreases, passes through a minimum, and then increases slowly, the total change in the conductivity for a considerable range in the dilution being surprisingly small. It may be that the salts undergo self-ionisation, and in the more concentrated solutions this effect would be greatest. As the solution is diluted the dissociation due to the salt itself would decrease, while that due to the solvent would increase. Finally, the dependence of the conductivity upon the two factors would exchange places, as it were, the decrease due to the weakening of the self-ionisation becoming less than the increase effected by the action of the solvent. It is by no means certain, however, that this is the correct explanation. Some of the results obtained by Franklin and Kraus are given in Table XI., v denoting the dilution in litres per gram-equivalent, *i.e.*, $v = \frac{1}{C}$, where C is the concentration expressed in gram-equivalents per litre.

The iodides of ammonia and of sodium have high equivalent conductance values for the more concentrated solutions, but on the other hand, potassium nitrate, ammonium chloride, and especially silver iodide, are distinguished by having low values for the more concentrated solutions.

Franklin and Kraus found that the alkali salts were less ionised in ammonia than in aqueous solutions of the same strength, but on calculating the degree of ionisation, α , from $\frac{\Lambda}{\Lambda_0}$ measurements, the values thus obtained were in accordance with Ostwald's dilution law. Potassium nitrate in a solution of dilution 3 litres per mole is less than 0.25 ionised, while in water, at the same concentration, 0.75 of the molecules of the salt are in the ionic condition. At a dilution of 1000 litres per mole, the salt in a

* *Amer. Chem. Jour.*, 23, 277 (1900).

TABLE XI.

EQUIVALENT CONDUCTANCE OF SALTS IN LIQUID AMMONIA AT -33°C .

Salt.	Dilution v .	Λ .	Salt.	Dilution v .	Λ .
AgCN	4.48	15.58	Hg(CN) ₂	3.37	1.86
	17.85	14.28		5.71	1.79
	69.69	12.83		21.8	1.63
	272.8	12.12		33.0	1.64
	1,063.0	12.00		55.6	1.75
LiNO ₃	25.88	118.0	NH ₄ Br	21.47	116.0
	109.8	155.5		87.40	152.5
	432.8	199.2		709.0	224.9
	1,703.0	236.5		1,407.0	251.0
	6,965.0	265.7		3,846.0	276.1
NaNO ₃	257.3	188.2	AgNO ₃	68.95	148.7
	1,352.0	246.0		186.6	181.7
	2,857.0	265.5		734.5	226.4
	5,150.0	278.7		2,892.0	259.5
	10,120.0	291.5		5,740.0	271.0
NaCl	66.3	121.8	Ba(NO ₃) ₂	358.0	147.2
	258.5	170.2		1,407.0	200.6
	1,008.0	223.0		7,542.0	280.0
	3,930.0	268.8		29,647.0	366.9
	30,330.0	307.0		58,750.0	422.5

solution of ammonia is still less than 0.75 dissociated, but in water, at the same concentration, ionisation is practically complete.

Water has a marked superiority over liquid ammonia as an ionising agent, and in the latter solvent the anions exert a greater influence upon the ionisation than the cations, for the iodides are conspicuously the most highly ionised of the salts. A curious fact is that in water the potassium salts are more highly ionised than those of sodium and of ammonium, but in liquid ammonia the potassium salts are least dissociated, *i.e.*, potassium nitrate and potassium bromide are ionised to a less extent, respectively, than the corresponding sodium and ammonium salts.

Franklin and Kraus found that the variation of the equilibrium constant, K , in dilute liquid ammonia solutions is much less marked than in the case of aqueous solutions and, apparently, dilute solutions in ammonia follow the mass action law more nearly than solutions of the same salts in water. Kraus and Bray* concluded that the concentration at which deviations from the dilution formula become appreciable is lower the greater the ionisation of the electrolyte. The values which these experimenters

* *Jour. Amer. Chem. Soc.*, 35, 1315 (1913).

obtained for K and Λ_0 with different electrolytes in liquid ammonia at -33°C . are shown in Table XII.:—

TABLE XII.

VALUES OF K AND OF Λ_0 FOR ELECTROLYTES IN LIQUID AMMONIA AT -33°C .

Salt.	$K \times 10^4$.	Λ_0 .	Salt.	$K \times 10^4$.	Λ_0 .
NaNH_2	0.56	263	NaNO_2	23.0	301
KNH_2	1.20	301	NH_4Br	23.0	303
AgI	2.90	287	LiNO_3	26.0	283
NH_4Cl	12.0	310	NaBr	27.0	302
NaCl	14.5	309	NaI	28.0	301
KNO_3	15.5	339	AgNO_3	28.0	287
KBr	21.0	340	NH_4NO_3	28.0	302
NaBrO_3	23.0	278	KI	42.0	339

Kraus and Bray * also determined the ionic mobilities at infinite dilution of various ions in liquid ammonia at -33°C . Their results are given in Table XIII. and, for the sake of comparison, the corresponding values in aqueous solutions are tabulated. It will be observed that in all cases the mobility in the ammonia solution is much greater than in water.

TABLE XIII.

IONIC MOBILITIES IN LIQUID AMMONIA AT -33°C .

Kation.	Ionic Mobility.			Anion.	Ionic Mobility.		
	In Ammonia.	In Water at 18°C .	Ratio.		In Ammonia.	In Water at 18°C .	Ratio.
Li^+	112	33.3	3.36	NH_2^-	133	—	—
Ag^+	116	54.0	2.15	BrO_3^-	148	47.6	3.11
Na^+	130	43.4	3.00	NO_3^-	171	61.8	2.77
NH_4^+	131	64.7	2.03	I^-	171	66.6	2.57
Ti^+	152	65.9	2.31	Cl^-	179	65.5	2.73
K^+	168	64.5	2.61	Br^-	172	67.7	2.54

34. Conductivity of liquid sulphur dioxide solutions.—In the liquid form pure sulphur dioxide has a conductivity about equal to that of water. The halogen salts mostly dissolve in it, and Walden and Centnerszwer † found that a remarkable regularity exists in the behaviour of the various salts which they investigated, although the regularity was by no means identical with that exhibited by the corresponding aqueous solutions. The

* *Loc. cit.*

† *Zeits. phys. Chem.*, 39, 513 (1902).

salts investigated were the chlorides, bromides, iodides and thiocyanates of potassium, sodium, rubidium, ammonium, mono-, di-, tri-, and tetramethyl ammonia, as well as ethyl and benzyl bases. For a dilution of 1 gram-equivalent in 1024 litres of aqueous solution their values of the equivalent conductance at 0° C. range between 50 and 80, but in sulphur dioxide they vary from 12 to 163. This difference does not appear to be due to varying degrees of ionisation. Franklin * also measured the equivalent conductance of solutions formed by dissolving potassium iodide, potassium bromide and tetramethylammonium iodide, respectively, in liquid sulphur dioxide. Some of his results at different temperatures are given in Table XIV., v being the dilution in litres per gram-equivalent.

TABLE XIV.

EQUIVALENT CONDUCTANCE OF SALTS IN LIQUID SULPHUR DIOXIDE.

Dilution v .	Equivalent Conductance at				
	- 33·5° C.	- 20° C.	- 10° C.	0° C.	10° C.
<i>Potassium Iodide.</i>					
1·0	37·7	44·1	46·9	51·2	54·5
4·0	40·5	43·4	44·8	45·5	46·0
8·0	41·0	42·0	42·5	42·0	41·4
32·0	47·2	48·3	47·8	46·4	44·5
128·0	65·9	66·9	66·5	64·5	62·0
256·0	78·8	81·8	81·7	79·4	76·5
512·0	93·4	98·2	99·2	98·0	95·3
1,000·0	108·6	115·2	118·8	119·4	117·7
8,000·0	153·0	168·5	181·8	189·0	196·0
16,000·0	163·0	184·0	199·0	211·0	223·0
<i>Potassium Bromide.</i>					
0·5	26·4	32·8	37·4	—	—
2·0	32·3	34·3	35·4	36·1	35·4
24·0	34·7	34·0	32·3	30·7	28·1
96·0	48·3	47·0	44·7	42·3	39·0
384·0	72·4	72·0	69·9	66·8	61·7
1,000·0	94·7	97·7	96·0	92·5	86·7
4,000·0	132·0	138·0	142·3	142·5	139·3
<i>Tetramethylammonium Iodide.</i>					
0·375	25·0	31·5	37·8	41·6	46·5
0·5	40·3	45·7	52·5	56·7	63·3
4·0	75·0	82·8	89·5	93·5	97·5
32·0	82·0	87·5	94·2	96·7	99·5
256·0	109·5	119·3	126·7	132·0	136·5
1,026·0	128·6	144·0	158·0	166·2	176·0

* *Jour. Phys. Chem.*, 15, 675 (1911).

increasing dilution. Kahlenberg and Ruhoff* found this to be characteristic of silver nitrate solutions in amylamine. Walden† has observed similar behaviour on the part of tetraethylammonium iodide solutions in acetaldehyde and acetic acid, and Shinn‡ with lithium chloride solutions in ethylamine. Sachanov and Prscheborowsky§ investigated the conductance of various electrolytes in different solvents of small specific inductive capacity. Many of these electrolytes showed maxima values in very concentrated solutions, but in no case was a minimum value observed. The decrease in molecular conductance with increasing concentration, as shown by extremely concentrated solutions of silver nitrate in aniline, has been ascribed by Kraus|| to the influence of increasing solution viscosity.

Kraus and Bray¶ determined the conductance of various electrolytes in acetone and in pyridine, both at 18° C. Their results are tabulated in Table XVI. :—

TABLE XVI.

EQUIVALENT CONDUCTANCE OF SALTS IN ACETONE AND IN PYRIDINE.

Acetone.				Pyridine.	
Salt.	Λ_0 .	Salt.	Λ_0 .	Salt.	Λ_0 .
KI	156	KBr	156	NaI	57.0
NaI	156	NaBr	156	KI	59.5
LiI	154	LiBr	154	KSCN	62.5
NH ₄ I	159	NH ₄ Br	159	NaSCN	60.0
KSCN	169	LiNO ₃	125	—	—
LiSCN	167	AgNO ₃	100	—	—
NH ₄ SCN	172	LiCl	154	—	—

The results show that, as in the case of ammonia, the conductance values at infinite dilution for the potassium salts in pyridine are considerably higher than those of the sodium salts. The conductance of the SCN⁻ ion is greater than that of the I⁻ ion, a result similar to that obtained in the case of acetone solutions.

Solutions in aniline are relatively poor conductors, but the conducting solution behaves generally like typical non-aqueous solutions. Pound** found that the molecular conductance in-

* *Jour. Phys. Chem.*, 7, 254 (1903).† *Zeits. phys. Chem.*, 54, 131 (1906).‡ *Jour. Phys. Chem.*, 11, 537 (1907).§ *Zeits. Elektroc.*, 20, 39 (1914).|| *Jour. Amer. Chem. Soc.*, 36, 60 (1914).¶ *Ibid.*, 35, 1315 (1913).** *Jour. Phys. Chem.*, 31, 547 (1927).

creases rapidly with more concentrated solutions, while at very low concentrations some of the solutions behaved like aqueous solutions, the conductance rising to a limit at zero concentration. The stronger acids with aniline give solutions of which the conductivities tend to increase with time. Assuming that the initial conductivity is due to the formation of aniline salts, the subsequent formation of aniline, and liberation of water, will explain this increase of conductivity.

Philip and Oakley * investigated the conductivity of potassium iodide in nitromethane at 25° C. They obtained the following results :—

Dilution in litres per mole	82.90	200.9	408.0	1673	4915	10082
Values of the conductance, Λ	85.14	98.06	105.5	115.82	119.27	120.47

Martin † measured the conductance, at 25° C., of solutions of lithium iodide, sodium iodide, potassium iodide, lithium bromide, and silver nitrate in benzonitrile over a range of dilution from 500 to 50,000 litres per mole. His results are given in Table XVII., the dilution being expressed, as usual, in litres per gram-equivalent.

TABLE XVII.

EQUIVALENT CONDUCTANCE OF SALTS IN BENZONITRILE.

Salt.	Dilution.	Λ .	Salt.	Dilution.	Λ .
KI	802.4	42.82	LiBr	498.1	11.38
	1,185	44.40		1,004	14.70
	4,543	48.30		4,941	25.47
	14,774	49.70		8,323	28.17
NaI	39,188	50.45		10,114	29.25
	484.5	37.98	AgNO ₃	39.86	7.50
	895.8	40.99		159.4	12.30
	5,384	45.29		724.6	22.18
	17,830	46.46		21,972	45.79
LiI	60,781	46.97		41,278	47.28
	103.1	24.91			
	943.3	38.14			
	2,340	41.72			
	4,648	43.18			
	9,719	44.00			

37. Mass action law for non-aqueous solutions.—We have seen that in the case of non-aqueous solutions, a large amount of experimental evidence has been collected which indicates that electrolytes in these solvents obey a law very different from that applicable to aqueous solutions. Thus, as we have noted, in

* *Jour. Chem. Soc.*, 125, 1189 (1924).† *Ibid.*, 132, 3270 (1928).

certain solvents the molecular conductance increases with rising concentration. Kraus and Bray,* however, have shown that uni-univalent salts in liquid ammonia, and also in certain alcohol solvents, do conform to the law of mass action provided that the solutions are dilute. Keyes and Winninghoff,† working with the iodides of sodium and ammonium in isoamyl alcohol, and also with sodium iodide in propyl alcohol, obtained similar results, even when the concentration of the solutions reached 0.0004 normal.

The highly ionised solutions of sodium, phenyl ammonium, potassium and ammonium formates in anhydrous formic acid also obey the mass action law up to concentrations of 0.3—0.6 normal. Schlesinger and Martin‡ determined the equilibrium constants of these salts to be 0.816, 0.814, 1.02 and 1.23, respectively. At concentrations greater than those mentioned, the formates deviate from the law in the sense that the degree of ionisation is less than it should be. This is the type of variation which would be expected from the kinetic theory, if the cause of the deviation lies in the reduction of the free space by the volume occupied by the solute itself.

Schlesinger and Coleman§ also found that solutions of lithium, rubidium and caesium formates in anhydrous formic acid followed Ostwald's dilution law over a fairly large range of concentrations. Furthermore, all the conductivity data agree with the demands of the law if the degree of ionisation is calculated from the equation $\alpha = \frac{A}{A_0}$.

Kraus and Bray|| examined the applicability of Ostwald's dilution law to dilute solutions of strong electrolytes in non-aqueous solvents, including the higher alcohols, and found that below ionic concentrations of 0.0001 normal the law applies within the limits of experimental error, but at higher concentrations deviations become measurable. This limiting ion-concentration is approximately the same for solutions of a given electrolyte in different solvents, and for different (strong or weak) electrolytes in the same solvent.

38. Conductivity of alkali metals in liquid ammonia.—Solutions formed by dissolving the alkali metals in liquid ammonia are good conductors of electricity. Kraus¶ has measured the conductance of these solutions, and it seems that the conduction

* *Jour. Amer. Chem. Soc.*, **35**, 1315 (1913).

† *Ibid.*, **36**, 1589 (1914).

|| *Loc. cit.*

‡ *Ibid.*, **38**, 1178 (1916).

§ *Ibid.*, **38**, 271 (1916).

¶ *Ibid.*, **43**, 749 (1921).

process is an ionic one, the metallic ion being positively charged and moving towards the kathode. There appears to be a negative carrier which is instrumental in conveying a part of the current through the solution, but when discharged at the anode, does not give any indication of a product at this electrode. In dilute solutions the equivalent conductance approaches a limiting value in a manner similar to that of ordinary electrolytes. At a concentration of, approximately, 0.05 normal the equivalent conductance has a minimum value, after which it begins to increase rapidly with rising concentration. This increase is particularly prominent in the neighbourhood of normal concentration and would seem to correspond to an increase in the relative speed of the negative carrier. A 2-normal solution of sodium in liquid ammonia has an equivalent conductance of 83,000, approximately. The negative carrier is identical for all metals and exhibits abnormal conducting power in the case of the more concentrated solutions. The equivalent conductances of the various solutions, as measured by Kraus at -33°C. , are given in Table XVIII., v being the dilution in litres per gram atom of metal.

TABLE XVIII.

CONDUCTANCE OF SOLUTIONS OF THE ALKALI METALS IN LIQUID AMMONIA.

<i>Sodium.</i>							
v	1.438	16.08	37.04	80.65	389.1	1,945.0	9,750.0
Λ	1,429.0	477.5	491.7	565.2	800.4	938.7	957.2
<i>Potassium.</i>							
v	1.695	7.560	15.87	70.94	324.4	1,434.0	2,990.0
Λ	1,414.0	596.1	532.1	594.6	787.2	894.3	884.1
<i>Lithium.</i>							
v	0.4229	1.990	8.817	18.13	40.17	85.94	181.6
Λ	25,600.0	879.4	501.2	454.6	502.2	569.9	654.4

39. Conductivity of salts in mixed solvents.—The addition of a weak acid to an aqueous solution of a strong acid produces a small decrease in the specific conductivity.* In the

* See Kendall and Andrews, *Jour. Amer. Chem. Soc.*, 43, 1545 (1921).

cases of hydrochloric and nitric acids the effect is confined to solutions stronger than 0.005 normal. It is caused by the mobilities of the ions of the resultant salt being less than the mobilities of the ions of the strong acid which have disappeared during the formation of the salt.

The conductivity of hydrochloric acid solutions is unaffected by the presence of hydrogen sulphide, and in the same way saturation of hydrochloric acid or nitric acid solutions with other gases of a weakly acidic nature, such as carbon dioxide or acetylene involves no measurable change in their specific conductances. Kendall and Andrews noted that with solutions of salicylic acid in hydrochloric acid there was an increase in the specific conductivity of the latter. At low concentrations the effect is practically absent. Magnanini* observed that the addition of polyhydric alcohols, in small amounts, increased the specific conductivity of boric acid solutions owing to the formation of complex molecules which were readily ionised. Jones and Lindsay,† and Jones and Carroll‡ studied solutions of several salts in mixtures of methyl alcohol and water, measurements being made at 0° C. and at 25° C. and at various concentrations. They concluded that the minimum molecular conductance which occurs is caused primarily by the great increase in viscosity which results when the two components of the mixture are brought together. In some cases no such minimum occurred.

Pound§ investigated the specific conductivity of ether and 95.0 per cent., by weight, of sulphuric acid at 30° C. As the percentage weight of ether in the solution decreased the value of K , the equilibrium constant, increased.

Kieran|| measured the equivalent conductance of hydrochloric-acid solutions through a wide range of dilution in the presence of varying quantities of sucrose, the concentration of the latter being maintained constant in each series of measurements in order that the viscosity of the solutions might also remain constant whilst the dilution of the acid varied. It was found that while the behaviour of potassium chloride in the presence of sucrose was normal, in that the equivalent conductance increased regularly with increased dilution, the behaviour of hydrochloric acid was abnormal, the value of the equivalent conductance passing through a maximum in the region 300-500 litres per mole, and steadily falling thereafter with increasing dilution. A detailed examina-

* *Gazz. chem. Ital.*, 20, 441 (1890); 23, 197 (1893).

† *Amer. Chem. Jour.*, 28, 329 (1902).

‡ *Ibid.*, 32, 521 (1904).

§ *Jour. Chem. Soc.*, 121, 941 (1922).

|| *Trans. Farad. Soc.*, 18, 119 (1922).

tion of the results showed that the abnormal behaviour was due to minute traces of electrolytic impurity in the sucrose.

Goldschmidt * has found that when small amounts of water are added to solutions of strong acids in alcohols, the equivalent conductance of the solution is greatly reduced. This reduction appears to be due to the formation of a complex hydrogen ion whose speed is relatively slow. It is interesting to note that, on the addition of water to weak acid mixtures, the equivalent conductance is increased, and this increase is, in general, greater the weaker the acid. Lithium chloride in ethyl alcohol also shows a slight increase in conductance on the addition of water. This influence of water upon the conductance of electrolytes in different solutions is readily accounted for on the assumption that complex molecules are formed, the ionisation of which is greater than that of the non-hydrated electrolyte.

40. Conductivity of soap solutions.—McBain, Laing and Titley † measured the conductivity of nearly all the soap solutions which can be studied at 0° C., such as solutions of the potassium salts of the saturated fatty acids and of the sodium salts. The soap solutions exhibited considerable conductance, even in concentrated solutions. These experimenters consider that the ions may be aggregated to form the nucleus of a colloidal particle, the so-called *ionic micelle*, whilst retaining their equivalent electrical charges. Thus, the ionic micelle exhibits conductivity, in addition to mobility, to an extent even greater than that of the ion contained within it. Some of the results are shown in Table XIX., where N_w is the strength of the soap solution (weight normality), σ , Λ and α having their usual significance.

TABLE XIX.
CONDUCTANCE OF SOAP SOLUTIONS AT 18° C.

Potassium Laurate.				Sodium Oleate.			
N_w .	$\sigma \times 10^6$.	Λ .	α .	N_w .	$\sigma \times 10^6$.	Λ .	α .
2.000	59,470	43.14	0.505	0.600	11,040	21.67	0.337
1.500	51,310	45.80	0.536	0.100	1,922	20.46	0.318
0.750	30,320	47.21	0.553	0.050	996.6	20.59	0.320
0.400	16,220	44.22	0.518	0.010	295.6	30.09	0.468
0.100	4,311	44.03	0.516				
0.050	2,713	54.89	0.643				
0.010	753.9	75.44	0.883				

* *Zeits. phys. Chem.*, 89, 129 (1914).

† *Jour. Chem. Soc.*, 115, 1279 (1919).

41. Conductivity of fused electrolytes.—The internal ionisation of a solid salt is always complete, but the ions are not free to move past one another because of the great magnitude of the cohesive forces, which prevent the displacement of an ion from its equilibrium position within the crystal lattice. At the melting-point all ions are free to move, and we may imagine that fused salts are completely split up into free moving ions.* Arndt † drew the same conclusion on the basis of investigations relating the viscosity with the molecular conductance of the fused salt. There is evidence to show that the degree of ionisation of fused salts varies but slightly with temperature, the change in electrical conductivity being almost entirely due to changes in viscosity. This is to be expected, as all the ions present contribute to the conduction of the electricity. Solidification of a fused salt is accompanied by a very large fall in conductance, this fall being attributed to a great decrease in the ionic mobilities, and not to any change in the degree of ionisation. The specific conductivities of the solid salts, sodium and potassium chlorides, at different temperatures, are given in Table XX.‡

TABLE XX.

CONDUCTANCE OF SALTS IN THE SOLID STATE.

NaCl. Melting-point = 1083° (A).		KCl. Melting-point = 1063° (A).	
Absolute Temperature.	Specific Conductance ohm ⁻¹ × 10 ⁶ .	Absolute Temperature.	Specific Conductance. ohm ⁻¹ × 10 ⁶ .
903°	12.6	923°	6.5
923°	21.2	933°	8.4
943°	35.0	983°	28.8
983°	95.0	1,013°	59.6
1,023°	240.0	1,043°	133.0
1,073°	729.0	—	—

42. Conductivity and concentration.—It has been pointed out, previously, that strong electrolytes do not follow Ostwald's dilution law, and various formulæ have been suggested to represent the relation between the equivalent conductance of such a solution and its concentration. Kohlrausch,§ from his experiments on the conductance of the sulphates of magnesium, zinc, cadmium and copper, of calcium chromate and magnesium

* See Nernst, *Festschrift*, p. 226 (1912).

† *Zeits. Elektrochem.*, 13, 510, 809 (1907).

‡ See Benrath and Wainoff, *Zeits. phys. Chem.*, 77, 257 (1911).

§ *Sitz. Akad. Wiss. Berlin*, 1215 (1904).

oxalate, showed that the results obtained could be represented, below concentrations of 0.002 normal, by the equation,

$$\Lambda_0 = \Lambda + kC^{\frac{1}{2}}, \quad . \quad . \quad . \quad (51)$$

where k is a constant and C the concentration of the solute in the solution. This equation, however, did not represent the conductance curves in many cases, *e.g.*, the chlorides of barium, magnesium, and calcium, the nitrates of barium, strontium, calcium and lead, and the sulphates of potassium and lithium. For these electrolytes the equivalent conductance, within the concentration range 0.0005 to 0.2 normal, could be represented by the equation,

$$\Lambda_0 = \Lambda + k\Lambda^p C^{\frac{1}{2}}, \quad . \quad . \quad . \quad (52)$$

where p varies according to the electrolyte.

Rudolphi * suggested that the equilibrium constant, K , could be expressed by the equation,

$$K = \frac{\Lambda^2 C^{\frac{1}{2}}}{\Lambda_0 - \Lambda}.$$

He determined the value of K for a large number of salts and acids, and showed that it was dependent upon the nature of the electrolyte and of the solvent, but independent of the concentration and temperature. Van't Hoff † suggested that

$$K = \frac{\Lambda^{\frac{2}{3}} C^{\frac{1}{3}}}{\Lambda_0^{\frac{1}{3}} (\Lambda_0 - \Lambda)},$$

which leads to the result, $\frac{C_i^3}{C_s^3} = \text{constant}$, where C_i and C_s are the concentrations of the ions and non-dissociated molecules, respectively.

Storch ‡ suggested that the relationship between concentration and degree of ionisation could be expressed in the form,

$$\frac{(C\alpha)^n}{C(1 - \alpha)} = K, \quad . \quad . \quad . \quad (53)$$

where n varies according to the electrolyte. This equation, which may be written in the form,

$$\frac{C_i^n}{C_s} = K, \quad . \quad . \quad . \quad (54)$$

* *Zeits. phys. Chem.*, 17, 385 (1895).

† *Ibid.*, 18, 300 (1895).

‡ *Ibid.*, 19, 13 (1896).

has been found to express, with a considerable degree of accuracy, the relation between the degree of ionisation and the concentration of strong electrolytes over a considerable concentration range. The values of n which give the best results for all types of salts vary within the rather narrow limits, 1.4—1.6. For any given salt the value depends slightly upon the concentration, in general increasing as the dilution is raised.

The correctness of the equation adopted is of the greatest importance because its chief use is to determine, by extrapolation, the value of Λ_0 , the equivalent conductance at infinite dilution. This function must be known before the degree of electrolytic ionisation can be calculated from conductance measurements.

Now since $\alpha = \frac{\Lambda}{\Lambda_0}$, equation (53) may be written thus,

$$C^{n-1}\Lambda^n = K\Lambda_0^{n-1}(\Lambda_0 - \Lambda) = K'(\Lambda_0 - \Lambda),$$

or
$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{1}{K'\Lambda_0}(C\Lambda)^{n-1},$$

and it is evident that K' will be constant for that value of n which, when substituted in the equation, gives a linear relationship between $\frac{1}{\Lambda}$ and $(C\Lambda)^{n-1}$. Noyes and Falk* chose the value of

n so that the graph obtained by plotting $\frac{1}{\Lambda}$ against $(C\Lambda)^{n-1}$ was nearly a straight line, and two other graphs, corresponding to neighbouring values of n on opposite sides of the first line, were also drawn so as to aid the determination of the most probable point— $\frac{1}{\Lambda_0}$ —at which the graphs cut the $\frac{1}{\Lambda}$ axis. They obtained accurate values of Λ_0 and of the percentage ionisation for a large number of salts.

Abbott and Bray† have shown that, if the percentage ionisation of a salt solution is plotted against its ion concentration, the resulting curves for salts of the same valence type do not intersect. It is also found that the salts of a single valence type divide themselves into several distinct groups. Thus, of the univalent type salts in 0.1 normal solutions, the chlorides, bromides and iodides of the alkali metals are all ionised to the same extent. The nitrates, bromates and chlorates of the same metals are ionised to a less extent.

An example of this graphical method is shown in Fig. 8, the

* *Jour. Amer. Chem. Soc.*, 34, 454 (1912).

† *Ibid.*, 31, 729 (1909).

data of Bray and Hunt * for sodium chloride at 25° C. having been used in the calculation. Interpolation curves are drawn by plotting values for $n = 2.00, 1.60, 1.50, 1.45$ and 1.35 . All of the curves pass through the same point, where $C\Lambda = 1$, and when extrapolated they must meet on the $\frac{1}{\Lambda}$ axis. The problem is to determine where the curve, which appears to be the most linear, cuts the axis; then from this point the value of Λ_0 can be deter-

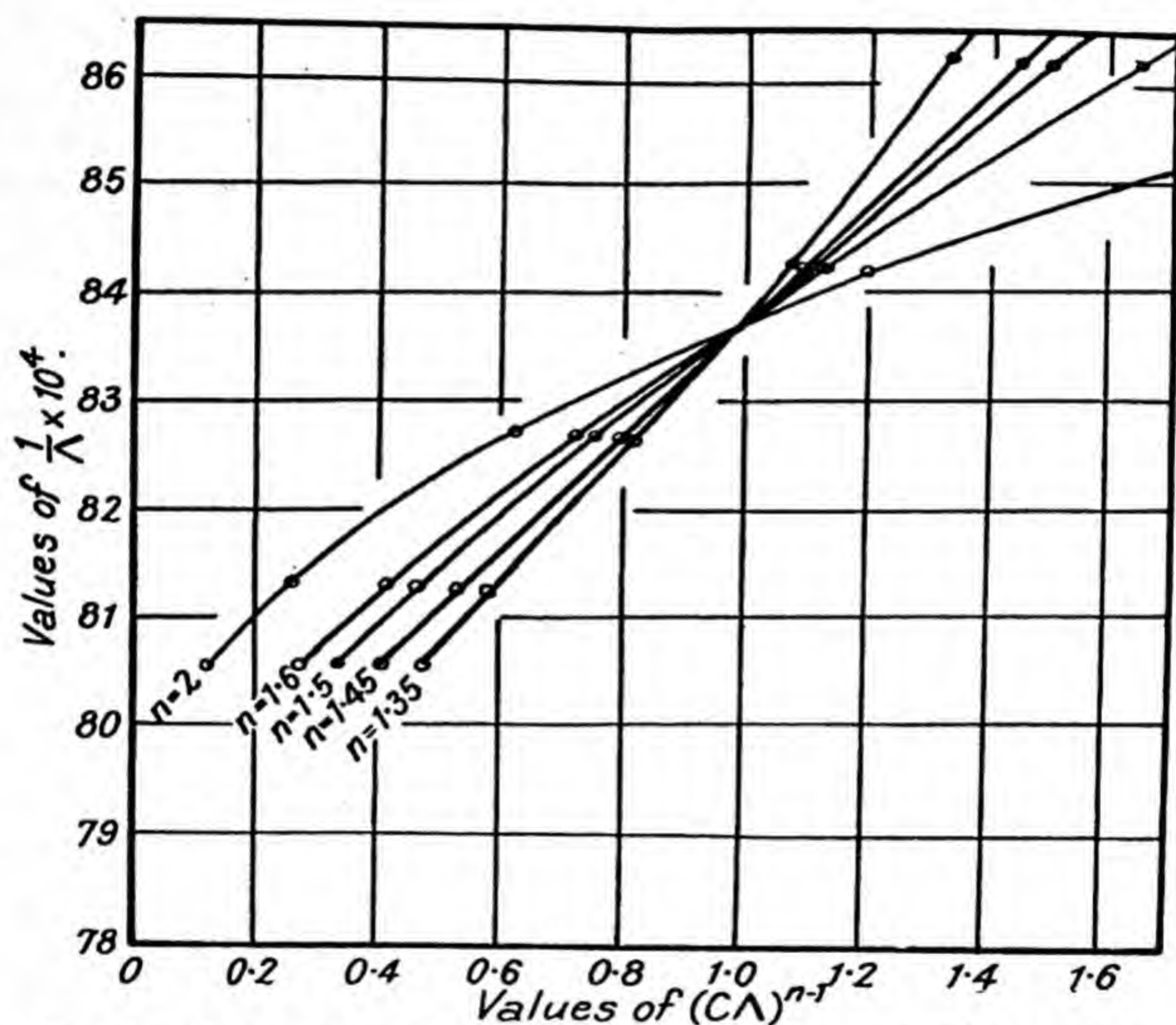


FIG. 8.—Graphical method of determining the value of Λ_0 (NaCl).

mined. In the figure the curve so chosen is that one corresponding to $n = 1.45$.

Bates † also used a graphical method to determine the value of Λ_0 . Differentiating equation (54) we have

$$nC_i^{n-1}dC_i = KdC_s,$$

or

$$n \frac{dC_i}{C_i} = \frac{dC_s}{C_s},$$

$$\text{i.e., } n d \log C_i = d \log C_s.$$

* *Jour. Amer. Chem. Soc.*, **33**, 781 (1911).

† *Ibid*, **35**, 519 (1913).

Hence, by plotting values of $\log C_s$, as abscissæ, against values of $\log C_i$, as ordinates, the slope of the tangent to the curve at any point is the value of n for the corresponding concentration. Using this method Bates found that in all cases, with decreasing concentration, n becomes more nearly equal to the value required by the law of mass action.

Washburn * plotted the relation between K and C for dilute solutions, where

$$K = \frac{C\Lambda^2}{\Lambda_0(\Lambda_0 - \Lambda)},$$

and assuming that Ostwald's law holds at infinite dilution, and that K is independent of C , he extrapolated the curve to the axis at zero concentration.

Lorenz † used the equation,

$$\Lambda = \Lambda_0 - kC^n, \quad . \quad . \quad . \quad (55)$$

and, taking Kohlrausch's value of Λ_0 for sodium chloride, he proceeded to calculate the values of k by giving n , in succession, the values 0.33, 0.40, 0.45, 0.50. He then found that for $n = 0.45$, the values of k over the range $C = 0.0001 - 0.02$ normal were fairly constant.

Ferguson and Vogel ‡ point out that this procedure is unnecessary. They consider equation (55) and plot values of Λ and C , a smooth curve being drawn through the points. They now choose a number of points whose abscissæ increase in any suitable geometrical progression, of common ratio, say r , and tabulate values of C , the corresponding values of Λ , and values of $\delta\Lambda$, the first difference. Thus,

$$\begin{aligned} \Lambda &= \Lambda_0 - kC^n, \\ \Lambda + \delta\Lambda &= \Lambda_0 - k(rC)^n, \\ \delta\Lambda &= kC^n(1 - r^n), \\ \text{and so} \quad \log \delta\Lambda &= \log k(1 - r^n) + n \log C. \\ \text{or} \end{aligned}$$

A curve drawn for the values of $\log \delta\Lambda$ and of $\log C$ gives a linear relationship which determines k and n , and so for every pair of values of Λ and C equation (55) enabled them to find a series of values of Λ_0 , of which the resulting mean gives the most probable value. As an example, they quote the results for an aqueous solution of potassium chloride at 18° C.

* *Jour. Amer. Chem. Soc.*, 40, 122 (1918).

† *Zeits. anorg. Chem.*, 108, 191 (1919).

‡ *Phil. Mag.*, 50, 971 (1925).

C. Gram-equivalents per litre.	Λ .	$\delta\Lambda$.	$\log \delta\Lambda$.	$\log C$.
1.0×10^{-4}	129.07			
2.0×10^{-4}	128.77	.30	$\bar{1}.47712$	$\bar{4}.00000$
4.0×10^{-4}	128.29	.48	$\bar{1}.68124$	$\bar{4}.30103$
8.0×10^{-4}	127.60	.69	$\bar{1}.83885$	$\bar{4}.60206$
1.6×10^{-3}	126.67	.93	$\bar{1}.96848$	$\bar{4}.90309$
3.2×10^{-3}	125.44	1.23	.08991	$\bar{3}.20412$
6.4×10^{-3}	123.77	1.67	.22272	$\bar{3}.50515$

A plot of $\log \delta\Lambda$ against $\log C$ gives $n = 0.4520$ and $k = 61.26$, so that for an aqueous solution of potassium chloride,

$$\Lambda = \Lambda_0 - 61.26 C^{0.4520}.$$

From any pair of observed values of Λ and C they now calculate Λ_0 . The results of this calculation are shown below, and it will be seen that the values of Λ_0 thus obtained are very consistent.

C	Λ	Λ_0 .
1.0×10^{-4}	129.07	130.02
2.0×10^{-4}	128.77	130.07
5.0×10^{-4}	128.11	130.08
1.0×10^{-3}	127.34	130.04
2.0×10^{-3}	126.31	130.00
5.0×10^{-3}	124.41	130.00
1.0×10^{-2}	122.43	130.07

TABLE XXI.

EQUIVALENT CONDUCTANCE OF AQUEOUS SOLUTIONS AT 18° C. (FERGUSON AND VOGEL.)

Salt.	Λ_0 .	k .	n .	Salt.	Λ_0 .	k .	n .
KCl	130.04	61.26	.4520	KCNS	121.08	74.35	.4947
NaCl	109.02	54.24	.4431	CsCl	133.07	80.97	.5062
LiCl	99.07	51.74	.4364	AgNO ₃	116.19	64.17	.4404
KNO ₃	126.39	74.67	.4796	KClO ₃	119.57	70.86	.4747
NaNO ₃	105.48	57.32	.4458	Ca(NO ₃) ₂	114.02	100.63	.4196
LiNO ₃	95.40	47.96	.4253	Sr(NO ₃) ₂	113.49	121.72	.4582
KIO ₃	98.54	61.07	.4604	Ba(NO ₃) ₂	116.87	175.63	.5120
NaIO ₃	77.54	54.66	.4551	Pb(NO ₃) ₂	123.44	164.50	.4520
LiIO ₃	67.53	48.22	.4422	CaCl ₂	116.75	115.84	.4622
KBr	132.30	58.15	.4324	MgCl ₂	111.63	83.87	.3991
KI	130.66	60.86	.4636	K ₂ SO ₄	132.85	141.98	.4582
KF	111.54	56.34	.4409	K ₂ C ₂ O ₄	125.73	323.97	.6772
NaF	90.08	62.69	.4831	MgSO ₄	113.72	626.2	.5507
TiNO ₃	127.39	113.10	.5458	CuSO ₄	114.16	810.2	.5711
TiCl	131.04	152.73	.5763	CdSO ₄	114.70	771.5	.5511

As the authors point out, they do not suggest that equation (55) is correct, but they use it entirely to calculate Λ_0 . Incidentally, however, they find that the equation is valid up to concentrations of 10^{-3} normal for all of the strong electrolytes investigated. For many uni-univalent and uni-bivalent electrolytes it holds up to a concentration of 0.01 normal. Since their calculations of the values of Λ_0 are probably the most accurate now available, the

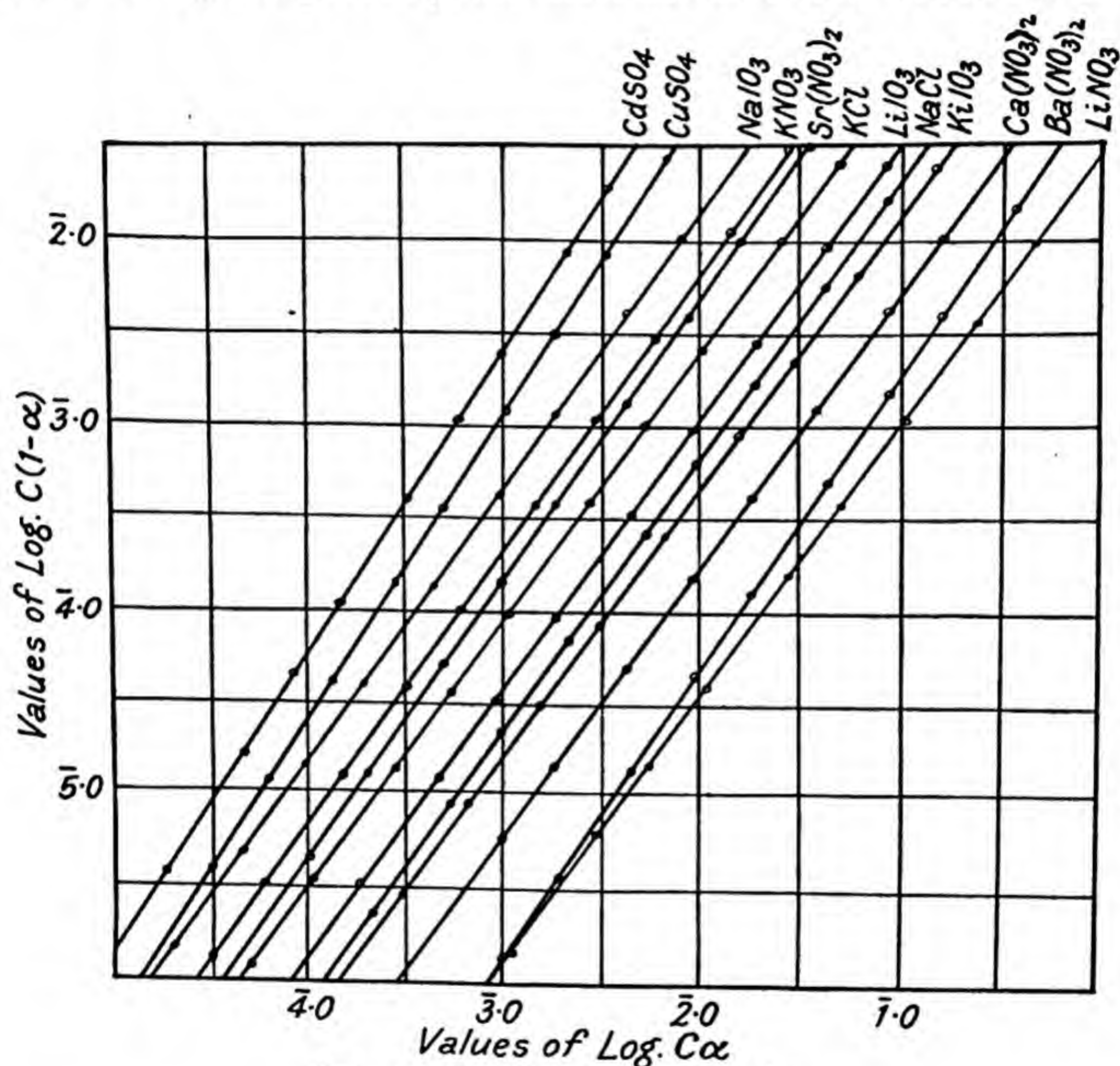


FIG. 9.—Storch's dilution equation.

values of Λ_0 , k and n for several electrolytes are given in Table XXI. Using these values they proceeded to test the validity of the simple Storch equation by a logarithmic plot of equation (55). Fig. 9 exhibits graphically the results for some substances, and the closeness with which the solutions follow this law is measured by the rectilinearity of the line drawn through the observed points.

The authors compared their values of Λ_0 with those calculated

by means of equations (51) and (52). The values of Λ_0 obtained from equation (52) fall off slightly with increasing dilution, and this deviation becomes more pronounced as the valency of the electrolyte increases. Thus, this equation (52) is not suitable for calculating the equivalent conductance at infinite dilution.

A perusal of the results shown in Table XXI. indicates that, contrary to the usual assumption that n is independent of the nature of the electrolyte, both k and n vary in a regular manner with the character of the electrolyte, and their values are therefore important characteristics of each electrolyte. It seems that k varies irregularly with the temperature, and n apparently decreases with rising temperature, except in the cases of potassium bromide and sodium acetate. Vogel* obtained the following values of n at different temperatures for a solution of potassium iodide in nitromethane:—

Temperature.	Λ_0 .	k .	n .
0° C.	90.79	353.8	.5726
25°	123.02	659.6	.6083
40°	144.1	717.6	.5939
55°	165.27	1,034.5	.6317
70°	193.0	928.6	.5552

Having determined the values of k and n , it is possible to calculate a value for the equilibrium constant, K , in Storch's equation, and the values thus computed serve to test the closeness with which Storch's law is followed. The values of K , calculated for several electrolytes by Ferguson and Vogel,† are given in Table XXII. From these results the variation in the value of n with concentration may be determined. For various

TABLE XXII.

CALCULATED VALUES OF THE EQUILIBRIUM CONSTANT, K , FOR DIFFERENT ELECTROLYTES AT 18° C. (FERGUSON AND VOGEL.)

Salt.	Values of K at Concentration.						
	10^{-4} N.	5×10^{-4} N.	10^{-3} N.	5×10^{-3} N.	10^{-2} N.	10^{-1} N.	N.
LiCl	1.50	1.54	1.56	1.55	1.54	1.57	1.44
LiNO ₃	1.64	1.66	1.66	1.63	1.62	1.61	1.44
Sr(NO ₃) ₂	0.68	0.69	0.68	0.67	0.67	0.68	0.58
Ba(NO ₃) ₂	0.49	0.50	0.50	0.48	0.48	0.48	—
CuSO ₄	0.068	0.069	0.068	0.065	0.065	0.077	0.112
CdSO ₄	0.056	0.059	0.059	0.058	0.058	0.068	0.093
HCl (25° C.)	0.094	0.092	0.102	0.158	—	—	—
HIO ₃ (25° C.)	0.073	0.072	0.075	0.097	0.113	0.180	—

* *Phil. Mag.*, 5, 199 (1928).

† *Ibid.*, 4, 1 (1927).

substances n is a linear function of the concentration, increasing as the concentration is raised. This result is directly opposed to the conclusions of Noyes and Falk,* and especially of Bates,† who stated that the values of n increase as the concentration falls.

It is of course possible that these results of Ferguson and Vogel are capable of other interpretations. The fact that an empirical equation will fit given sets of figures is no guarantee that it is the correct equation to apply, and it is obvious that the good agreement obtained by these experimenters, by varying the values of k and n , can equally well be obtained by using other empirical equations. Nevertheless, Ferguson and Vogel have refuted the claim that the simple square root formula (51) of Kohlrausch best represents the relation between the equivalent conductance of strong electrolytes and concentration. It is evident that the correctness, or otherwise, with which a formula represents this dependence varies with the accuracy of the experimental data.

Assuming that ionisation is complete in dilute solutions, and that the motion of an ion through a solvent obeys Stokes's law, Debye and Huckel ‡ deduced the expression

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left(\frac{k_1 \omega_1}{D^{\frac{1}{2}}} + \frac{k_2 \omega_2 b}{D^{\frac{1}{2}}} \right) \sqrt{nC}, \quad . \quad . \quad (56)$$

where k_1 and k_2 are universal constants for all solvents at the same temperature,

D , the specific inductive capacity of the solvent,

ω_1 and ω_2 are termed valency factors,

b , the harmonic mean of the ionic radii,

n , the number of ions per molecule, and

C , the equivalent concentration of the electrolyte.

The values of ω_1 and ω_2 , for different salt types in which the anion and kation have equal mobilities, are given below; ω_1 varies with the relative mobilities of the two ions, but ω_2 is independent of these mobilities:—

Salt type.	Values of Valency Factors	
	(ω_1).	(ω_2).
KCl	1	1
K ₂ SO ₄	4.24	1.41
MgSO ₄	8	2

Equation (56) may be written in the form

$$\Lambda_0 = \Lambda + kC^{\frac{1}{2}},$$

* *Jour. Amer. Chem. Soc.*, 34, 479 (1912).

† *Ibid.*, 35, 519 (1913).

‡ *Phys. Zeits.*, 24, 305 (1923).

where k is determined in terms of certain constants of the electrolyte and solvent, and the exponential of C is independent of the nature of the electrolyte. The formula thus agrees with equation (51), but not with the results of Ferguson and Vogel, since these experimenters show that n is not constant. The equation is in general agreement with experimental results for strong electrolytes, as the change in the equivalent conductance, Λ , is proportional to the square root of the concentration. It is also dependent upon the dielectric constant of the solvent and upon the valencies of the ions. The best test of the theory is to see how nearly the equation enables us to calculate the equi-

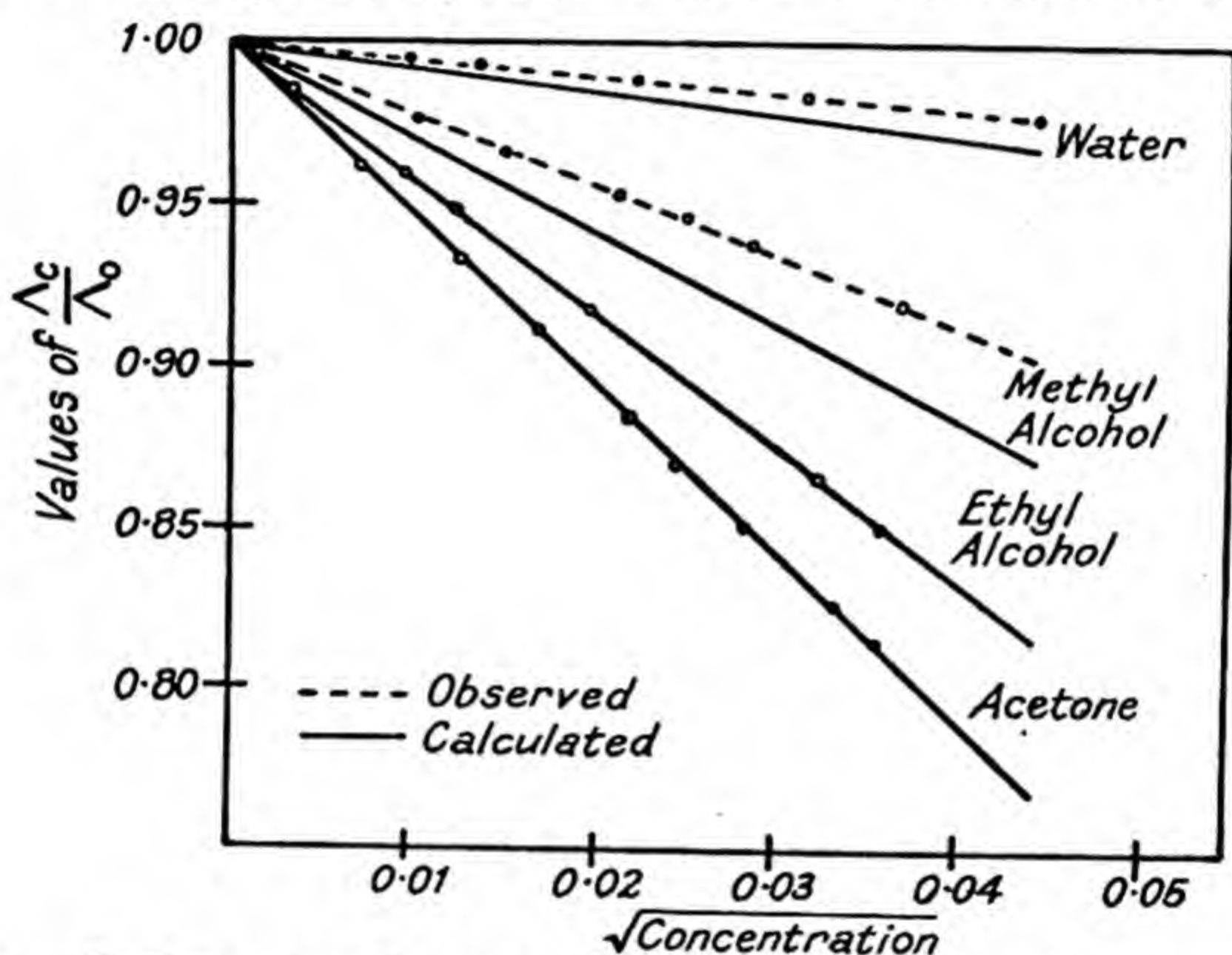


FIG. 10.—Equivalent conductance of potassium iodide in different solvents.

valent conductance of a salt in different solvents. Hartley* plotted observed and calculated values for potassium iodide in various solvents, the values of b required being calculated, by means of Stokes's law, from the ionic mobilities at infinite dilution. The results are shown in Fig. 10, and it will be seen that in water and methyl alcohol the calculated slope of the $\frac{\Lambda_c}{\Lambda_0}$ curve is greater than the observed slope, but in ethyl alcohol and acetone the agreement is very close. Other salts give better agreement in some solvents than in others, but it is a remarkable achievement that the theory predicts so closely the variation of the equivalent conductance of electrolytes, in

* *Nature*, 119, 322 (1927).

dilute solutions of different solvents, from a knowledge of the physical properties of the solvent and the ionic mobilities at infinite dilution.

Hartley and Frazer* have shown that Debye and Huckel's equation holds for eighteen uni-univalent salts in methyl alcohol below a concentration 0.002 normal, and subsequent work has confirmed it for a large number of other salts. Walden, Ulich and Busch† have found the same relationship for salts in acetone below 0.0005 normal, while Ulich has recently used the square root law in recalculating the values of the equivalent conductance at infinite dilution of electrolytes in a number of solvents. Debye and Huckel also examined a large number of experimental results for many non-aqueous solvents, and found that, in general, the more accurate and concordant the data, the more closely did they conform to the square root relation in dilute solution.

The dilution at which the linear relationship ceases varies with the solvent, the solute and the temperature. It is interesting to note that in some non-aqueous solvents, certain lithium salts do not obey the relationship, or do so only at exceptionally high dilution. There is little doubt that the exceptional behaviour of these salts is due to the formation of complex ions.

Duperthius‡ measured the conductance of salts in pyridine and in various alcohols between 0° C. and 80° C., and his results show that the range of applicability of the square root relation is diminished at the higher temperatures.

As mentioned previously, Hartley and Frazer, by means of Debye and Huckel's formula, calculated values of the equivalent conductance at infinite dilution of different salts in methyl alcohol at 25° C. Vogel,§ using Hartley and Frazer's experimental results, but Ferguson and Vogel's method of calculating values of Λ_0 , determined the values of Λ_0 in methyl alcohol.

Table XXIII. shows the comparison between the two sets of results and, as will be noted, there are several discrepancies.

Onsager,|| assuming complete ionisation in dilute solutions, deduced the equation,

$$\Lambda = \Lambda_0 - \beta\sqrt{\gamma}, \quad . \quad . \quad . \quad (57)$$

where $\gamma = (\nu_1 + \nu_2)C$, and

$$\beta = \frac{0.986 \times 10^6}{(DT)^{\frac{1}{2}}} \cdot w\Lambda_0 + \frac{29.0}{(DT)^{\frac{1}{2}}\eta}(\nu_1 + \nu_2).$$

* *Proc. Roy. Soc., A*, 109, 351 (1925).

† *Zeits. phys. Chem.*, 123, 429 (1926).

‡ Dissertation, Lausanne (1908).

§ *Phil. Mag.* 5, 199 (1928).

|| *Phys. Zeits.*, 27, 388 (1926).

TABLE XXIII.

EQUIVALENT CONDUCTANCE OF SALTS IN METHYL ALCOHOL AT 25° C.

Salt.	Λ_0 (Vogel's Value).	k .	n .	Λ_0 (Frazer and Hartley's Value).
LiCl	89.92	447.6	.6213	90.90
NaCl	97.29	192.3	.4670	90.95
KCl	104.96	271.2	.5074	105.05
RbCl	109.41	209.0	.4448	108.65
CsCl	113.78	275.2	.4882	113.60
LiNO ₃	100.22	240.7	.4926	100.25
NaNO ₃	106.00	363.5	.5409	106.45
RbNO ₃	117.20	495.8	.5604	118.15
CsNO ₃	123.24	373.3	.4930	122.95
AgNO ₃	109.97	1066.1	.6591	112.95
KBr	109.20	300.3	.5226	109.35
KI	114.38	331.4	.5422	114.85

D is the dielectric constant of the solvent, ν_1 and ν_2 the valencies of the anions and kations, respectively, η the coefficient of viscosity of the solution, and

$$w = \nu_1 \nu_2 \cdot \frac{2q}{1 + \sqrt{q}},$$

q being given by

$$q = \frac{\nu_1 \nu_2 (U_0 + V_0)}{(\nu_1 + \nu_2)(\nu_2 U_0 + \nu_1 V_0)}.$$

U_0 and V_0 are the mobilities of the ions at infinite dilution. When the solvent is water at 18° C.,

$$\beta = 0.27w\Lambda_0 + 17.85(\nu_1 + \nu_2).$$

For uni-univalent electrolytes in water at 18° C.,

$$\beta = 35.7 + 0.159\Lambda_0.$$

Fig. 11 shows the relation between measured and calculated values of the conductivity at different concentrations. The individual differences between the electrolytes are chiefly given by the limiting slopes of the curves, hydrochloric acid showing the greatest absolute, and smallest relative, decrease of equivalent conductivity, Λ , with increasing concentration, lithium iodate the greatest relative, and smallest absolute, decrease.

Onsager has determined values of β from the conductivity measurements of Kohlrausch, and compared the results with the values of β calculated from the value of Λ_0 . The deviations of the calculated from the theoretical values are very small for

uni-univalent electrolytes, so it is concluded that Onsager's equation applies to this type of electrolyte.

For bivalent binary electrolytes in water,

$$\Lambda = \Lambda_0 - \beta\sqrt{4\gamma}, \quad . \quad . \quad . \quad (58)$$

where $\beta = 71.4 + 0.636\Lambda_0$.

Davies,* using Onsager's equation for uni-univalent electrolytes, such as salts of the alkali metals, finds that the salts are almost completely ionised up to concentrations of 0.5 normal.

Lattey† suggested that for strong electrolytes,

$$\Lambda_0 - \Lambda = \frac{A}{B + v^{\frac{1}{2}}}, \quad . \quad . \quad . \quad (59)$$

where A and B are constants peculiar to the solution in question,

and v is the dilution in gram-equivalents per litre. He calculated the equivalent conductance of potassium chloride solutions at different concentrations, and found that equation (59) gave results to within $\frac{1}{10}$ per cent. of the measured values even with normal solutions. The other formulæ which have been suggested for strong electrolytes break down at values of v between 20 and 50.

In an attempt to find a general expression for the relation between the concentration and the degree of ionisation which is applicable to all electrolytic solutions, Kraus and Bray‡ suggested the formula,

$$\frac{(C\alpha)^2}{C(1-\alpha)} = K + k(\alpha C)^n, \quad (60)$$

in which K , k and n are constants determined both by the nature of the electrolyte and of the solvent.

In sufficiently dilute solutions the term involving $(\alpha C)^n$ becomes negligible in comparison with K , and the equation approaches the simple mass action law as a

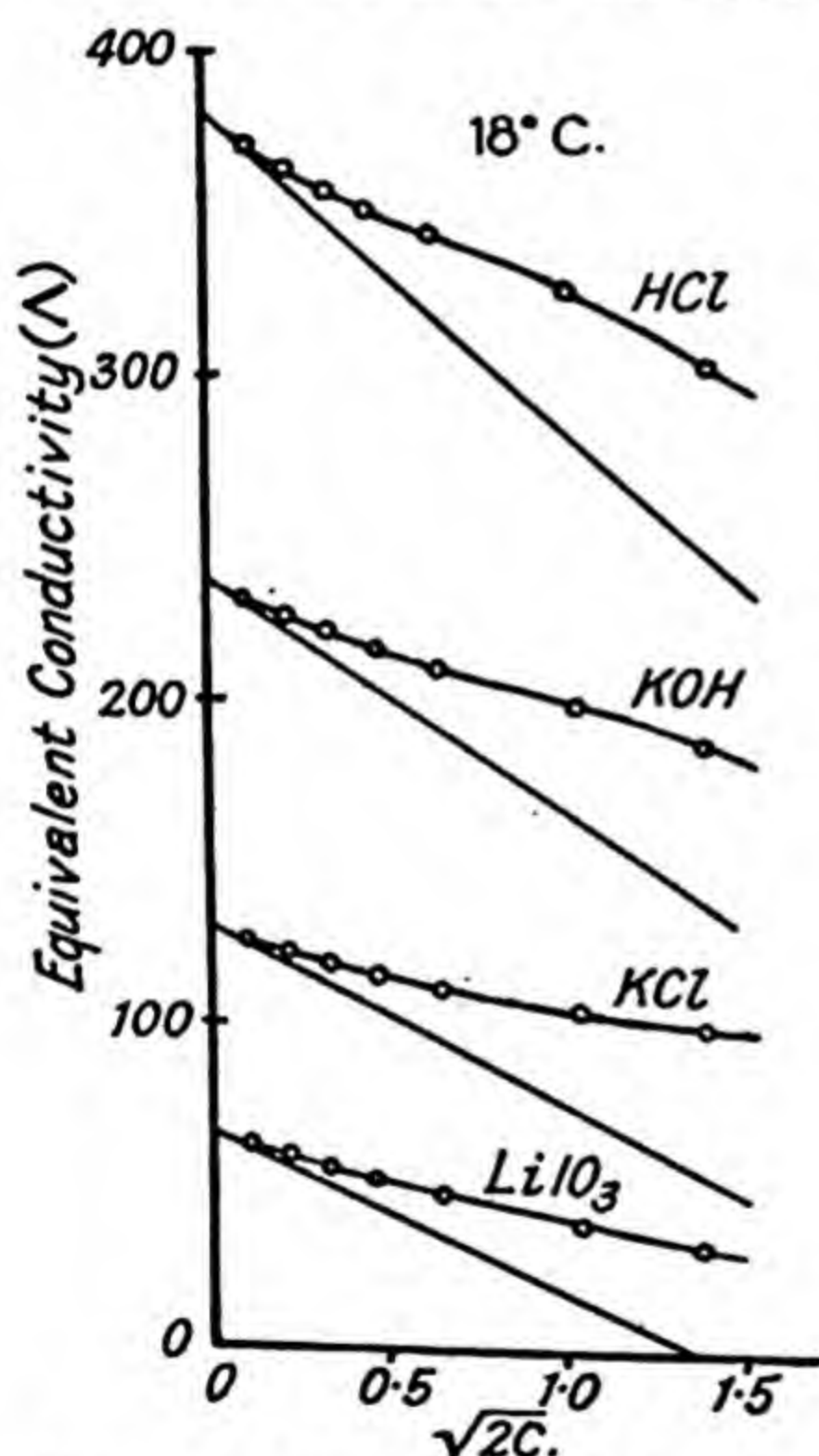


FIG. 11.—Equivalent conductance of electrolytes in water. (Onsager's formula.)

* *Trans. Farad. Soc.*, 23, 355 (1927).

† *Phil. Mag.*, 4, 831 (1927).

‡ *Jour. Amer. Chem. Soc.*, 35, 1315 (1913).

limit. In concentrated solutions K becomes negligible in comparison with $k(\alpha C)^n$, and the equation assumes the form of Storch's equation. For values of $n > 1$ the molecular conductance passes through a minimum value, while for values of $n < 1$ the molecular conductance decreases continuously with increasing concentration. The general equation applies to the data available for solutions in liquid ammonia and liquid sulphur dioxide. These experimenters examined the applicability of the mass action law to dilute solutions of strong electrolytes in non-aqueous solvents, and found that up to ionic concentrations between 0.0001 and 0.001 normal, the law applies within the limits of experimental error, but at higher ionic concentrations the deviations become measurable. This limiting ionic concentration is approximately the same for solutions of a given electrolyte in different solvents, and for different electrolytes in the same solvent.

Szyszkowski * suggested the equation,

$$\frac{(C\alpha)^2}{C(1-\alpha)} = K + k[C(1-\alpha)]^n, \quad (61)$$

to represent the variation of ionisation with concentration. This equation is similar to equation (60), the only difference being that the deviations from the mass action law are attributed in one case to the influence of the ions, and in equation (61), to the influence of the non-dissociated molecules. The fact that the ionisation reaches a minimum value at a certain concentration is, perhaps, more readily interpreted in terms of Szyszkowski's formula. Recently † he has proposed another formula which is in good agreement with experimental facts over a wide range of concentrations.

43. The relation between conductivity and viscosity.—

The ions in their motion through a solvent are subjected to a viscous drag, or retarding force, due to the viscous properties of the solvent. Wiedemann ‡ first suggested that the conductance of an electrolytic solution is dependent upon its viscosity, and he inferred that if the relationship is a simple one, the conduction process must consist of a migration of carriers through the solution, under the influence of the impressed potential difference and against the opposing frictional resistance of the surrounding molecules. The mobility of the ions depends, therefore, upon the fluidity § of the medium through which they

* *Medd. Nobel. Inst.*, 3, No. 2 (1915).

† *Acad. Pol. Sci. et Lettres Bull.*, 8a, 324 (1926).

‡ *Pogg. Ann.*, 99, 228 (1856).

§ Fluidity is the inverse of viscosity, i.e., $f = \frac{1}{\eta}$.

travel. When the temperature, or concentration, of a solution is altered, there is usually a marked alteration in the fluidity, and experimental data point to the conclusion that this produces a change in the ionic mobilities which may, as a first approximation, be justly regarded as proportional to the change of fluidity, so that $U = af$, $V = bf$, and $U + V = (a + b)f$, where a and b are constants and f is the fluidity of the medium.

In certain cases this simple linear relationship undoubtedly exists. Thus, in very dilute aqueous solutions the equivalent conductance is actually directly proportional to the fluidity over the range 0° - 36° C. Kohlrausch * has shown that this relationship also holds good for dilute solutions of sodium valerate, in which the mobility of one of the ions is very small. In other cases the linear relationship is less accurate, and although the ionic mobilities are closely related to the fluidity, they no longer obey a linear law. Thus Kohlrausch † found that the temperature coefficient of ionic mobility, $\frac{1}{U} \frac{dU}{dT}$, in dilute solutions is usually

less than the fluidity temperature coefficient, $\frac{1}{f} \frac{df}{dT}$, the difference being greatest for the hydrogen and hydroxyl ions. Wolf, ‡ and Rudorf § have also shown that when the viscosity of a salt solution is increased, at constant temperature, by the addition of acetic acid, or a non-electrolyte, the decrease in the conductivity is proportionally less than the decrease in fluidity.

Johnston || found that

$$\Lambda_0 = kf^a,$$

where k and a are constants, Λ_0 , the limiting equivalent conductance of a given electrolyte at any temperature, and f , the fluidity at the same temperature. He showed that a does not differ greatly from unity, being generally less than unity, and that it has a specific value for the individual ions. Washburn ¶ proposed to apply a correction for viscosity to the conductance of each ion, assuming that the change in speed which an ion experiences, as a result of a given viscosity change with concentration, is the same as that to which it is subjected for the same viscosity change, brought about by a change in temperature.

It is evident that in interpreting the viscosity influence on

* *Proc. Roy. Soc., A*, 71, 338 (1903).

† *Sitz. der Akad. Wiss. Berlin*, 26, 572 (1902).

‡ *Zeits. Elektroc.*, 8, 117 (1902).

§ *Zeits. phys. Chem.*, 43, 257 (1903).

|| *Jour. Amer. Chem. Soc.*, 31, 1010 (1909).

¶ *Ibid.*, 33, 1461 (1911).

conductance, the relative dimensions of the ions are of primary importance. Change in viscosity is, in general, produced in one of three ways, namely, by a change in the concentration, which may be due to the addition of either a new substance or a larger amount of one already present in solution; by a change in pressure, or by a change in the temperature. As the size of an ion increases it is probable that, ultimately, its speed will become a linear function of the fluidity. That its speed should change more rapidly than the fluidity seems unlikely, unless the dimensions of the ion change. Kraus has shown that for very large ions conductance and fluidity change in direct proportion to each other, but that for ions of smaller dimensions, the speed undergoes a relatively smaller change than the fluidity of the solvent, and this change is smaller the smaller the ion, *i.e.*, the larger the original speed of the ion.

It is a little doubtful whether Stokes's law is applicable to bodies as small as ions. Millikan * has investigated this law as applied to small particles, and has concluded that it can only be regarded as valid in liquids for spheres of radii greater than 10^{-6} cm. Most ions are considerably smaller than this.

The change of viscosity with concentration is much greater for inorganic electrolytes in non-aqueous solvents, than for the same electrolytes in water. The speed of the ions in non-aqueous solutions changes far less than the fluidity of the solutions, although at high concentrations the addition of a non-electrolyte, which produces a variation in the viscosity, also causes a change in the equivalent conductance in the same direction, but in most cases the variation of the equivalent conductance is less than the viscosity change. The smaller the molecules of the added non-electrolyte and the larger the ions, the more nearly does the equivalent conductance vary in direct proportion to the change of fluidity.

The relationship between the mobility of an ion, in a solution of appreciable concentration, and the actual fluidity of the solution, may be represented † by the scheme,

$$\text{change in } C \begin{cases} \nearrow \text{change in } X \\ \searrow \text{change in } f \end{cases} \text{change in } U,$$

where X indicates the forces acting on the ions and the other symbols have their aforementioned meaning. This relationship shows the necessity of applying a viscosity correction to experi-

* The Electron.

† See Allmand, *Trans. Farad. Soc.*, 23, 350 (1927).

mentally determined values of the mobilities. The value of this correction may be obtained as follows. If we assume that the results obtained from equation (42), *viz.*,

$$\Lambda = \alpha(u_A + u_K)F, \quad \Lambda_0 = (u_A + u_K)_0 F,$$

are correct, the suffix ₀ referring to infinite dilution, then,

$$\alpha = \frac{\Lambda}{\Lambda_0} \frac{(u_A + u_K)_0}{u_A + u_K},$$

so, assuming that

$$\frac{(u_A + u_K)_0}{u_A + u_K} = \frac{\text{fluidity at infinite dilution}}{\text{fluidity at given dilution}},$$

and remembering that the fluidities are inversely proportional to the coefficients of viscosity, we have

$$\alpha = \frac{\Lambda}{\Lambda_0} \cdot \frac{\eta}{\eta_0}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (62)$$

where η and η_0 are the coefficients of viscosity of the solution at the given concentration and at infinite dilution, respectively. This general formula is not exactly true. A more accurate relationship is that given by the equation,

$$\alpha = \frac{\Lambda}{\Lambda_0} \cdot \left(\frac{\eta}{\eta_0}\right)^k, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (63)$$

where k is a constant, the value of which depends upon the electrolyte. Nevertheless, k is, in most cases, so nearly unity, and its exact determination is a matter of such difficulty, that we may assume, with Noyes,* that equation (62) is sufficiently accurate. The whole correction for changes in mobility is small except for solutions of considerable concentration, and thus any error in the correction applied will produce a much smaller error, proportionally, in the values deduced both for the corrected equivalent conductance and the coefficient of ionisation. The values of this correction at different concentrations for aqueous solutions of sodium and potassium chlorides, at 18° C., are given in Table XXIV.† The concentrations are expressed in gram-equivalents per litre.

A most important relationship, known as *Walden's rule*, was found by Walden ‡ to exist between the equivalent conductance of

* See Noyes and Falk, *Jour. Amer. Chem. Soc.*, **34**, 454 (1912).

† *Ibid.*

‡ *Zeits. phys. Chem.*, **107**, 219 (1923); **114**, 297 (1924); **113**, 429 (1924).

TABLE XXIV.
EQUIVALENT CONDUCTANCE AND VISCOSITY.

Salt.	Concentration.	Λ .	$\frac{\eta}{\eta_0}$	$\Lambda \frac{\eta}{\eta_0}$	Salt.	Concentration.	Λ .	$\frac{\eta}{\eta_0}$	$\Lambda \frac{\eta}{\eta_0}$
NaCl	0.01N	101.88	1.0009	101.97	KCl	0.01N	122.37	—	122.37
	0.02N	99.55	1.0018	99.73		0.02N	119.90	0.9996	119.9
	0.05N	95.66	1.0046	96.10		0.05N	115.69	0.9991	115.6
	0.10N	91.96	1.0086	92.75		0.10N	111.97	0.9982	111.8
	0.20N	87.67	1.0167	89.13		0.20N	107.90	0.9959	107.5
	0.50N	80.89	1.041	84.13		0.50N	102.36	0.9898	101.3
	1.00N	74.31	1.086	80.70		1.00N	98.22	0.982	96.5

a solution at infinite dilution and the coefficient of viscosity of the solvent, *viz.*,

$$\Lambda_0 \eta = \text{constant} \quad . \quad . \quad . \quad . \quad (64)$$

the value of the constant being independent of the solvent's nature. This relationship is generally valid for salts which consist of large ions, presumably not admitting of rotation on account of their size. For such ions a similar relationship must exist between the ionic mobilities U_0 , V_0 , and the viscosity coefficient η , and it is only necessary to determine the product $U_0 \eta$ or $V_0 \eta$ for such an ion in water, in order to predict the mobilities of the ion in all other solvents. Ulich* has tested this relationship for a large number of solvents and different ions. The substance chosen for the initial calculation was the large ion, $\text{N}(\text{C}_2\text{H}_5)_4^+$, of tetraethyl ammonium salts, the mean value of $U_0 \eta$ for this ion in water being 0.295. The results at 25° C., given in Table XXV., show that in many cases there is approximate constancy of the products $U_0 \eta$ and $V_0 \eta$. This constancy cannot be accidental.

The importance of Walden's rule lies in the fact that by means of it the value of the equivalent conductance, at infinite dilution, of an electrolyte, in any solvent, may be calculated. This is especially useful in the case of those solutions for which it is not convenient to determine this quantity experimentally.

Onsager† used the empirical formula,

$$\frac{\Lambda_0 - \Lambda \eta^{0.5}}{(50.49 + 0.2238 \Lambda_0)} = f(C),$$

* *Trans. Farad. Soc*, 23, 388 (1927).

† *Ibid.*, 341 (1927).

TABLE XXV.

VALUES OF $U_0\eta$ AND $V_0\eta$ (WALDEN'S RULE).

Solvent.	Values of Ionic Conductance \times Viscosity for the Ion							
	$N(C_2H_5)_4^+$	$N(CH_3)_4^+$	Na^+	K^+	Cl^-	Br^-	I^-	CNS^-
Water	·295	·415	·459	·668	·682	·698	·686	·598
Methyl alcohol	·294	·354	·251	·292	·284	·305	·332	·327
Ethyl alcohol	·295	·317	·238	·267	·232	·244	·285	·28
Acetone	·294	·325	·217	·220	·332	·370	·366	·40
Furfural	·293	—	·190	·215	—	—	·424	—
Acetonitrile	·294	—	·28	·31	—	·35	·38	·44
Epichlorhydrin	·295	·338	—	—	·328	·363	·365	—
Pyridine	·294	—	·22	·27	—	—	·42	·45

Solvent.	H^+	Li^+	Ag^+	NH_4^+	$\frac{1}{2}Ba^{++}$	NO_3^-	ClO_4^-	Picrate $^-$
Methyl alcohol	·779	·213	·284	·322	—	·832	·376	·267
Ethyl alcohol	·669	·192	·185	·24	—	·282	—	·263
Acetone	—	·224	—	·278	·270	—	·365	·266
Water	3·14	·347	·569	·664	·58	·634	·616	·269

to represent the behaviour of various electrolytes, η being the relative viscosity of the solution. The values found for $f(C)$ are given below :—

$C = 0.005N$	$0.01N$	$0.02N$	$0.05N$	$0.1N$
$f(C) = 0.07006$	0.09441	0.1246	0.1748	0.2239

The equation is approximately true for some electrolytes even up to concentrations 0.5 normal.

Lattey * proposed the formula

$$U_0 = a + \frac{b}{\eta}$$

to represent the relation between the mobility of an ion and the viscosity of the solution, a and b being constants. His results for different electrolytes are shown in Fig. 12, and except for electrolytes containing H^+ and OH^- ions, the calculated and experimentally determined values of Λ_0 agree.

Another interesting relation between the equivalent conductance at infinite dilution and the viscosity of the solvent is that, if the motions of the ions are in accordance with Stoke's law, and if the ions are of the same size, the ratio of the values of Λ_0 for

* *Trans. Farad. Soc.*, 23, 412 (1927).

a given salt in two solvents should equal the ratio of the fluidities of the solvents. This has been shown by Martin* to be true for salts in benzonitrile and in methyl alcohol solutions. His results are as follows, $\frac{\eta(\text{MeOH})}{\eta(\text{PhCN})}$ being equal to 0.45.

Solute	KI	NaI	LiI	LiBr	AgNO ₃
$\frac{\Lambda_0(\text{PhCN})}{\Lambda_0(\text{MeOH})}$.45	.45	.47	.38	.46

44. Conductivity and temperature.—In the majority of cases the value of the ionisation coefficient, α , is found to decrease

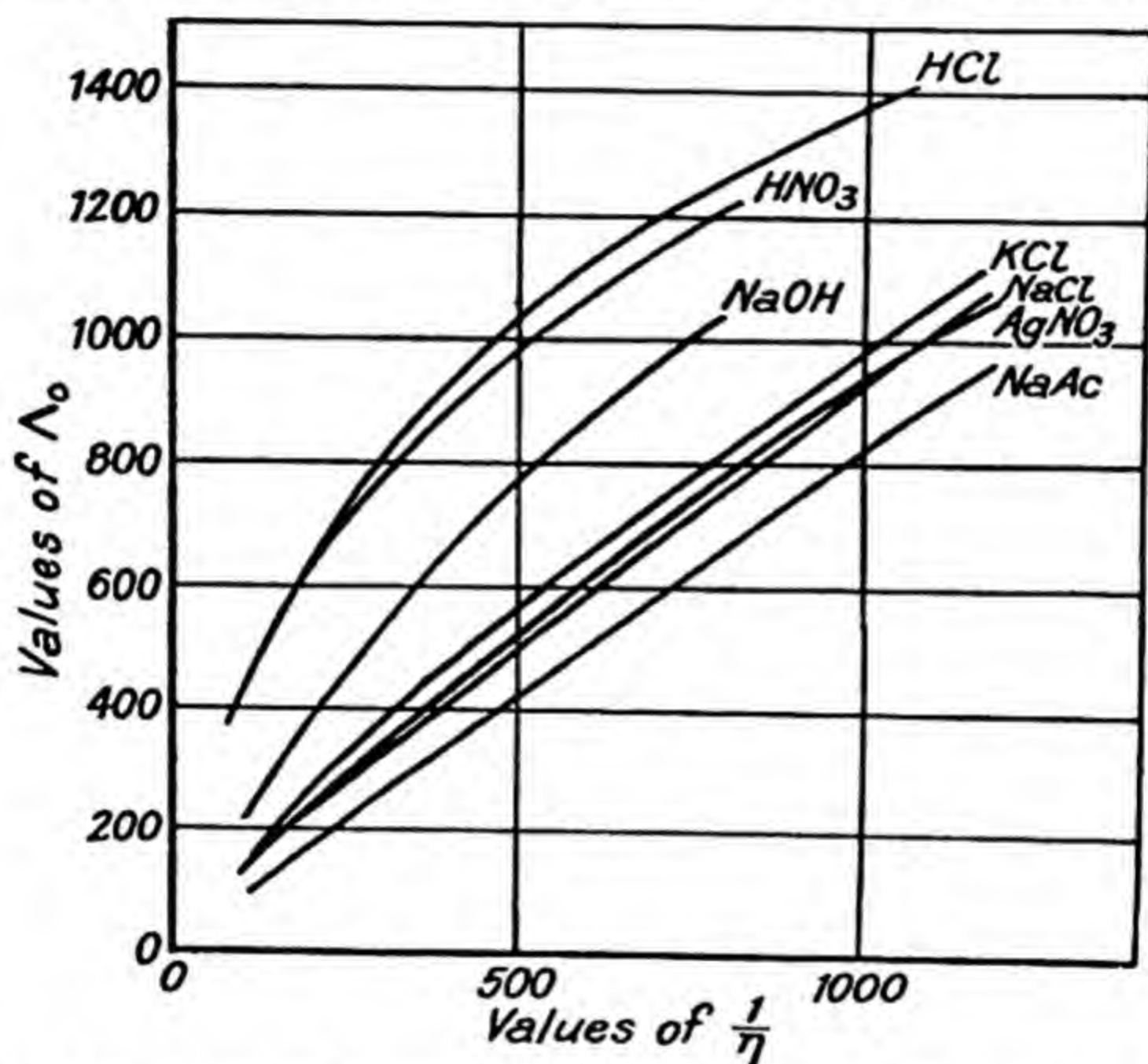


FIG. 12.—Variation of equivalent conductance of electrolytes in water with fluidity.

as the temperature rises, and the primary effect of an increase of temperature is therefore to reduce the amount of active material in the solution. On the other hand, the equivalent conductance at infinite dilution invariably increases as the temperature is raised. This is due to an increase in the mobilities of the ions, and is intimately related to the decreasing viscosity of the solution, the ionic migration proceeding more rapidly as the temperature rises. The temperature effect on the equivalent conductance is therefore determined by two opposing influences,

* *Jour. Chem. Soc.*, 132, 3270 (1928).

and the temperature coefficient, $\frac{1}{\Lambda} \frac{d\Lambda}{dT}$, will be positive or negative, according as one or other of these influences predominates.

In the case of aqueous solutions the temperature coefficient, at 18° C., is always positive. The conductivity-temperature coefficient curves are very flat, and may be represented by the linear equation,

$$\Lambda_t = \Lambda_{t_0} (1 + at), \quad . \quad . \quad . \quad (65)$$

where t is measured in degrees C., and a is the temperature coefficient. The curves, however, are more accurately represented by the formula,

$$\Lambda_t = \Lambda_{t_0} (1 + at + bt^2), \quad . \quad . \quad . \quad (66)$$

Λ_t and Λ_{t_0} being the equivalent conductances at t° C. and 0° C., respectively.

The influence of temperature on the conductivity of aqueous solutions has been investigated by many workers and Kohlrausch,* from observations in the case of dilute solutions, deduced the temperature coefficients of many infinitely dilute solutions. He proposed the formula,

$$\sigma_t = \sigma_{18} [1 + a(t - 18) + b(t - 18)^2], \quad . \quad (67)$$

where σ_t and σ_{18} are the specific conductances at t° C. and 18° C., respectively. His values of a and b for different electrolytes in water are given in Table XXVI.

TABLE XXVI.

TEMPERATURE COEFFICIENTS OF ELECTROLYTIC SOLUTIONS (AQUEOUS).

Electrolyte.	a .	b .	Electrolyte.	a .	b .
HNO ₃	·0163	— ·000016	K ₂ SO ₄	0·0222	+ ·000077
HCl	·0164	— ·000015	Pb(NO ₃) ₂	·0224	+ ·000078
H ₂ SO ₄	·0165	— ·000017	BaCl ₂	·0225	+ ·000083
H ₃ PO ₄	·0169	— ·000001	NaCl	·0226	+ ·000084
KOH	·0190	+ ·000032	SrSO ₄	·0228	+ ·000084
KNO ₃	·0210	+ ·000062	Na ₂ SO ₄	·0233	+ ·000097
KI	·0212	+ ·000058	MgSO ₄	·0238	+ ·000095
AgNO ₃	·0216	+ ·000067	NaHC ₄ H ₄ O ₄	·0241	+ ·000109
KCl	·0217	+ ·000067	NaF	·0242	+ ·000102
NH ₄ Cl	·0219	+ ·000068	NaC ₂ H ₃ O ₂	·0242	+ ·000110
NaNO ₃	·0220	+ ·000075	NaC ₅ H ₉ O ₂	·0243	+ ·000111
Ba(NO ₃) ₂	·0220	+ ·000075	Na ₂ CO ₃	·0262	+ ·000151
KF	·0222	+ ·000079			

* Preuss, *Akad. Wiss. Berlin, Sitz. Ber.*, 42, 1026 (1901). See also Bousfield and Lowry, *Proc. Roy. Soc., A*, 71, 42 (1902).

As a increases b is seen to increase regularly, from a small negative value in the case of acids, to a comparatively large positive value, and the relationship between the constants may be expressed, within the limits of experimental error, by the formula,

$$b = 0.0163(a - 0.0174). \quad (68)$$

A similar equation was also used by Kohlrausch to express the influence of temperature on the individual ionic mobilities.

Negative values of b occur only with the H^+ ion for which $a = +0.0154$, $b = -0.000033$, and so with the acids which contain this ion. Positive values of b range from that of the hydroxyl ion,

$$a = +0.0179, b = +0.000008,$$

to that of the lithium ion,

$$a = +0.0261, b = +0.000155.$$

Since b can be evaluated when a is known, the change of conductivity with temperature may be expressed in terms of a single arbitrary constant. When $a = 0.174$, $b = 0$, from equation (68), and the conductivity temperature curve is then a straight line. The two constants in equation (68) are nearly equal, and the experimental results may be represented, with only slightly less accuracy, by means of the formula,

$$b = 0.0177(a - 0.0177).$$

According to this formula the conductivity of all salt solutions should cease at $-39^\circ C.$, whilst the more accurate formula gives the variation in the conductance zero of $\pm 2^\circ C.$ according to the nature of the salt. Now the viscosity coefficient, η , of water may be represented by the formula,

$$\eta = 2.989(t + 38.5)^{-1.40}.$$

It would appear, therefore, that at $-39^\circ C.$ water entirely loses its fluidity, and a ready explanation of the conductance zero of aqueous solutions is afforded. Bousfield and Lowry* criticised the actual existence of such a sharply defined critical temperature, and considered that even at temperatures considerably lower than $-39^\circ C.$, the electrolytic solution might still retain some appreciable conductivity.

In the case of incompletely dissociated solutions Kohlrausch found that the relation between a and b , given by equation (68), is less exact, but that this equation has a remarkably wide range; a fair agreement appears, even in the extreme case of $KHSO_4$,

* *Loc. cit.*

where, for a 5 per cent. solution, a is 0.0095, and also in the case of sulphuric acid where a changes from 0.0125, in a 5 per cent. solution, to 0.0345 in an 84.5 per cent. solution, whilst b changes in the normal way from -0.000052 to $+0.000297$.

The striking agreement between the constants in the equations relating the change of conductance and of fluidity with temperature shows that, not only do the conductance and the fluidity of very dilute aqueous solutions tend towards zero values at the same limiting temperature, but also that their variation with temperature can be expressed by one formula, and represented by one curve. In apparent contradiction to this statement, is the fact that for acids and acid salts in aqueous solution, the temperature coefficient of conductance is actually smaller than the viscosity temperature coefficient of water, and that non-aqueous solvents have very small and even negative conductance temperature coefficients. Thus Malsch and Wien* have shown that when an electrolytic solution is traversed by current impulses of short duration, the measured temperature coefficient is not the normal value that accompanies prolonged heating. They found that with this sudden heating the temperature coefficient is essentially determined by that of the viscosity. It is the same for all ions in aqueous solution, *viz.*, 2.2 per cent. The ions are still unchanged and their movement obeys the friction laws. If the heating lasted a somewhat longer time, say 10^{-6} or 10^{-5} sec., changes of the temperature coefficient appear which, according to Kohlrausch's assumption, are attributable to changes in the constitution of the electrolyte.

Whilst at low temperatures the temperature coefficient of conductance is determined mainly by the changing ionic mobilities, at higher temperatures the variation in the degree of ionisation becomes the dominant factor, and it has been suggested that at high temperatures an upper limit may exist, at which the conductance would again become zero, owing to the complete absence of ionisation. In the case of aqueous solutions the indications of an upper conductivity zero are only slight, and measurements indicate that this upper zero conductivity point must lie very much farther from the boiling-point temperature than the lower zero conductance point is removed from the freezing-point temperature. We should expect a maximum conductivity as the temperature is raised, and these maxima have actually been observed by Sach† in the case of aqueous solutions of copper sulphate. For the majority of aqueous solutions the temperature of the

* *Phys. Zeits.*, 25, 559 (1924).

† *Wied. Ann.*, 43, 212 (1891).

conductance maximum lies above the boiling-point temperature, and experimental work is rendered very difficult.

Much more evidence is available for the existence of an upper zero conductivity value in the case of non-aqueous solutions. Franklin and Kraus * found that at high temperatures the conductance of solutions in liquid ammonia decreases as the temperature rises—an effect directly opposite to that observed by other workers. Maltby † has shown that even at atmospheric temperature, the conductance of an ethereal solution of hydrochloric acid decreases as the temperature rises. Negative temperature coefficients have also been observed by Cattaneo ‡ with solutions of ether, alcohol, and glycerol. Hagenbach § measured the conductivity of solutions in sulphur dioxide at temperatures ranging from 20° C. to 160° C. He found that the temperature coefficients, between 100° C. and 140° C., of sodium iodide, potassium chloride,

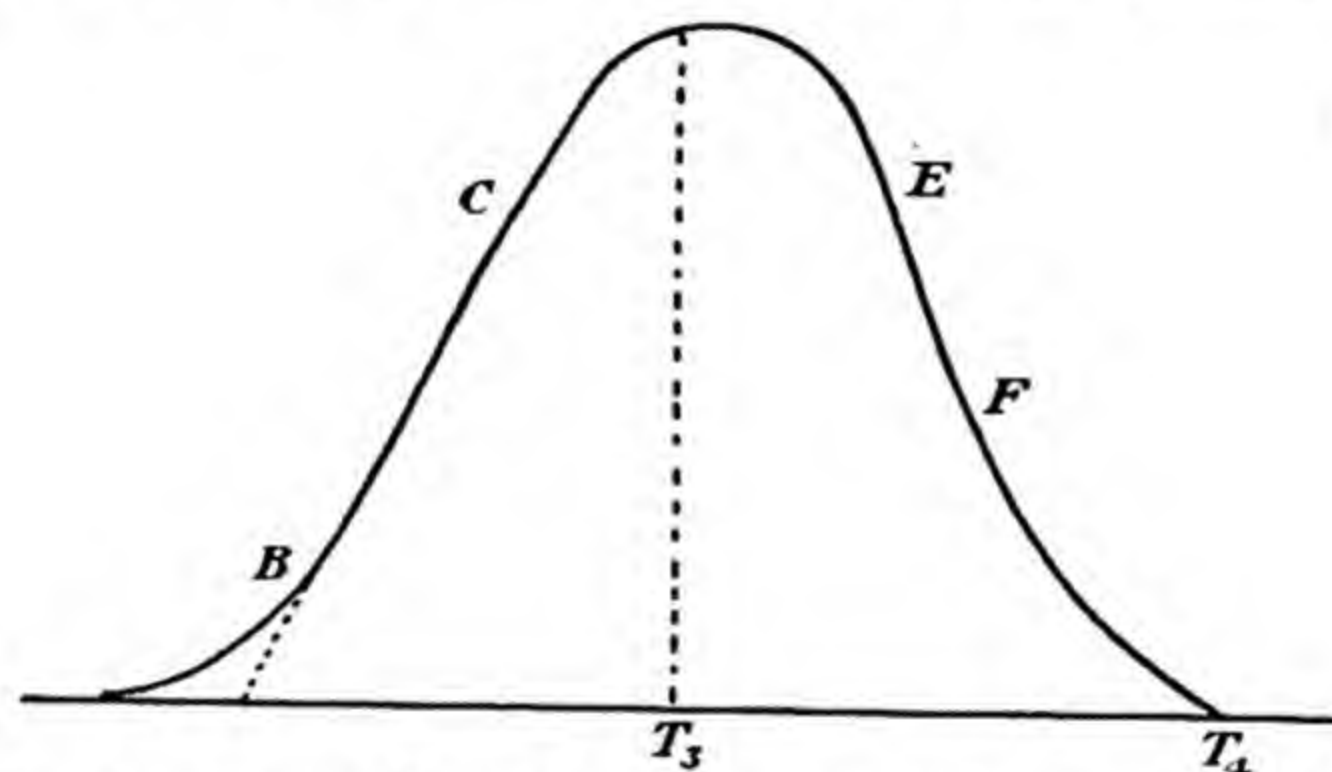


FIG. 13.—The influence of temperature on conductance.

potassium bromide and the iodide were all negative, and the temperature of the upper zero conductivity value of these solutions, determined by extrapolation, was in each case some 5° C. or 10° C. above the critical temperature of the solution.

High-temperature measurements have also been made by Walden and Centnerszwer || with solutions in sulphur dioxide, hydrochloric acid, quinoline, and a number of organic iodides.

Bousfield and Lowry ¶ represent the influence of temperature on the conductance of an electrolytic solution by means of a curve such as is shown in Fig. 13. At some intermediate temperature, T_3 , the value of which depends upon the nature of the solute

* *Amer. Chem. Soc. Jour.*, 24, 83 (1900).

† *Zeits. phys. Chem.*, 18, 133 (1895).

‡ *Rend. Lincei*, 2, I, 295; II, 112 (1893).

§ *Ann. de Phys.*, 2, 276 (1901).

|| *Zeit. phys. Chem.*, 39, 549 (1902).

¶ *Loc. cit.*

and the solvent, as well as upon the concentration of the solution, the conductivity reaches a maximum. As the temperature falls, the conductance decreases, and over a considerable range, BC, the curve follows an approximately linear law, the line becoming concave to the temperature axis near C, and convex near B. On this part of the curve the conductivity of the majority of aqueous solutions is represented, the acids giving values on the concave, and the salts on the convex, part of the curve.

Above the maximum point the decreasing viscosity effect being now more than counterbalanced by that due to the decreasing ionisation of the solution, the change in the degree of ionisation becomes more marked as the temperature rises, and the curve EF runs steadily down, cutting the axis at T_4 , the critical temperature of the solution, which is thus the temperature of the upper conductivity zero of the solution.

Kunz * measured the conductance of strong aqueous solutions of sulphuric acid of at least four gram-equivalents per litre. The conductance of the strongest solutions falls gradually with the temperature, attaining a relatively small value at -70°C . It is impossible to follow the more dilute solutions to so low a temperature on account of their freezing. It is evident, however, that the more dilute they are, the more rapid is the rate of change of the conductance with temperature.

We have already referred to the phenomenon of ion hydration. About every ion there moves an atmosphere of the solvent, the dimensions of this atmosphere being determined by the individual characteristics of the ion. The electrolytic resistance of a solution is a frictional resistance acting on the ions, and increases with the dimensions of the atmosphere. Thus the direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness.

The empirically discovered law, that the temperature change of resistance runs parallel to the change of the viscosity of water with temperature, may be explained on the hydration theory. As a limiting case, for a very slow moving ion, *i.e.*, one with a relatively thick water atmosphere, there is, during the motion of the ion through water, only friction of water against water, and therefore the electrolytic resistance will have the same temperature coefficient as that of the viscosity of water, provided that the atmosphere itself does not change its dimensions with temperature. If, however, the atmosphere decreases with increasing temperature, the temperature coefficient of conductance may

* *Comptes Rendus*, 135, 788 (1902).

become greater than that of the fluidity. In connection with this hydration process Jows* has pointed out that those ions with the greatest hydrating power have the largest conductivity temperature coefficients, and that those substances of equal hydrating power have also, approximately, the same temperature coefficients of conductance.

The complexes present in solutions break down at higher temperatures, and thus we should expect a greater increase in the conductivity of strongly hydrated salts as the temperature is raised than for substances but feebly hydrated. This conclusion has been verified by experiment,† but potassium ferricyanide and ammonium chromate form exceptions to the rule.

In conclusion, therefore, it seems that electrolytic resistance is due, in part at any rate, to a mechanical friction between an ion, or its atmosphere, and the surrounding solvent.

* *Amer. Chem. Jour.*, **34**, 357 (1905).

† See Watkins and Jones, *Jour. Amer. Chem. Soc.*, **37**, 2626 (1915).

BIBLIOGRAPHY.

- Bancroft, *Zeits. phys. Chem.*, **31**, 188 (1899).
 Böeseken and others, *Rec. trav. Chim.*, **35**, 211, 309 (1916).
 Bousfield, *Phil. Trans.*, A, 206, 101 (1906).
 Braune, *Zeits. phys. Chem.*, **85**, 170 (1913).
 Davies, *Jour. Phys. Chem.*, **29**, 986 (1925).
 Davis and Jones, *Zeits. phys. Chem.*, **81**, 68 (1913).
 Duperthus, *Dissertation*, Lausanne (1908).
 Dutoit and Levier, *Jour. Chim. Phys.*, **3**, 435 (1905).
 Dutoit and Rapoport, *ibid.*, **6**, 545 (1908).
 Fawsitt, *Proc. Roy. Soc., Edinburgh*, **25**, 51 (1904).
 Fitzgerald, *Jour. Phys. Chem.*, **16**, 621 (1912).
 Franklin, *Jour. Phys. Chem.*, **15**, 675 (1911); *Zeits. phys. Chem.*, **69**, 290 (1909).
 Franklin and Cady, *Jour. Amer. Chem. Soc.*, **26**, 499 (1904).
 Gagnaux, *Dissertation*, Lausanne (1907).
 Goldschmidt and Thuesen, *Zeits. phys. Chem.*, **81**, 30 (1912).
 Gorke, *Zeits. phys. Chem.*, **61**, 500 (1908).
 Green, *Jour. Chem. Soc.*, **93**, 2049 (1908).
 von Halban and Ebert, *Zeits. phys. Chem.*, **112**, 407 (1924).
 Hartley and Raikes, *Trans. Farad. Soc.*, **23**, 393 (1927).
 Hartley, Thomas and Appleby, *Jour. Chem. Soc.*, **93**, 538 (1908).
 Herzog, *Zeits. Elektroc.*, **16**, 1003 (1910).
 Jones, Carnegie publication, No. 8.
 Jones and Veazey, *Zeits. phys. Chem.*, **62**, 49 (1908).
 Jones, Bingham and McMaster, *Zeits. phys. Chem.*, **57**, 193 (1906).
 Kailan, *Zeits. phys. Chem.*, **89**, 678 (1915).
 Kendall, *Medd. K. Vetens. Nobelinstitut*, Bd. 2, No. 38 (1913).
 King and Partington, *Trans. Farad. Soc.*, **23**, 522 (1927).
 Kohlrausch and Gruneisen, *Berl. Ber.*, 1215 (1904); *Ges. Abh.*, **2**, 1078 (1911).
 Korber, *Zeits. phys. Chem.*, **67**, 222 (1909).
 Kraus, *Jour. Amer. Chem. Soc.*, **42**, 1 (1920); *Phys. Rev.*, **18**, 40 (1904).
 Kraus and Bishop, *Jour. Amer. Chem. Soc.*, **44**, 2206 (1922).
 Lorenz, *Zeits. anorg. Chem.*, **108**, 191 (1910); *Zeits. phys. Chem.*, **78**, 257 (1911).

- MacDougall, Jour. Amer. Chem. Soc., **34**, 855 (1912).
MacInnes and Cowperthwaite, Institute of Technology, Massachusetts, Contribution No. 19.
Martin and Masson, Jour. Chem. Soc., **79**, 707 (1901).
Morgan and Lammert, Jour. Amer. Chem. Soc., **46**, 1117 (1924).
Noyes and Falk, Jour. Amer. Chem. Soc., **33**, 1436 (1911).
Philip and Courtman, Jour. Chem. Soc., **97**, 1261 (1910).
Plotnikov and Rokotjan, Zeits. phys. Chem., **84**, 365 (1913).
Raikes, Yorke and Ewart, Jour. Chem. Soc., **128**, 630 (1926).
Rimbach and Weitzel, Zeits. phys. Chem., **79**, 279 (1912).
Sachanov and others, Zeits. Elektroc., **20**, 39 (1914); Zeits. phys. Chem., **87**, 441 (1914); J. Russ. Phys. Chem. Soc., **47**, 849 (1915).
Schlesinger and Bunting, Jour. Amer. Chem. Soc., **41**, 1934 (1919).
Schlesinger and Mullinix, Jour. Amer. Chem. Soc., **41**, 72 (1919).
Schlesinger and Reed, Jour. Amer. Chem. Soc., **41**, 1727 (1919).
Schmick, Zeits. f. Phys., **24**, 56 (1924).
Schmidt, Zeits. phys. Chem., **75**, 319 (1910).
Walden and Ulich, Zeits. phys. Chem., **106**, 49 (1923).
Walden, Zeits. Elektroc., **12**, 77 (1906); **26**, 65 (1920); Zeits. anorg. Chem., **115**, 49 (1920).
Wasastjerna, Soc. Sci. Fenn. Comm. Phys. Maths., **38**, 1 (1923).
Washburn, Jour. Amer. Chem. Soc., **40**, 150 (1918).
Whetham, Proc. Roy. Soc., A, **71**, 332 (1903).

CHAPTER IV.

THE MIGRATION OF THE IONS.

45. Material effects accompanying the conduction process.—We have already discussed the manner in which the conductance of an electrolyte depends upon the velocities and concentrations of the ions within the solution. The current is carried through the solution, partly by the anions, and in part by the kations, the ions arriving at the electrodes being deposited thereat. It is evident, therefore, that the strength of the solution must decrease unless the ions, which are removed at the electrodes, are replenished in some manner. This disappearance of the ions may be shown by passing an electric current between platinum electrodes through an aqueous solution of copper sulphate. The blue coloration gradually disappears, at first from the neighbourhood of the electrodes, and then extending towards the central portion of the solution. If the electrolysis is allowed to proceed for a sufficiently long period all of the copper ions are removed from the liquid.

Since they move towards the kathode there must be, at any rate within the neighbourhood of the anode, a loss in the concentration of these copper ions, and in general the greater the velocity of the ion, the more rapid will be the change in the concentration of this ion within the vicinity of the anode. It is obvious, therefore, that the changes in ionic concentration, brought about in this manner, must be a measure of the ionic velocity. Although the anions and kations usually move through a solution at different velocities, equivalent quantities of each ion always separate out at the anode and kathode, respectively, in accordance with Faraday's law of electrolysis. In other words, for every faraday of electricity which passes through an electrolytic solution one gram equivalent of kation is set free at the kathode and a gram equivalent of anion at the anode, irrespective of the ionic velocities.

It must be realised that there is a difference between the manner in which the current is conveyed from one layer of the solution to the next, and that in which it is conveyed from the liquid to either electrode. Within the liquid the transference is partly

by positive ions travelling in one direction, and partly by negative ions travelling in the opposite direction, whereas, at the electrodes the transference is by means of one kind only—by positive ions at the kathode and by means of negative ions at the anode. In consequence of this, more kations are deposited at the kathode, and more anions at the anode, than those for which the ionic streams, due to the applied potential gradient, are responsible.

46. Concentration changes produced by current.—Hittorf* first investigated the part which each ion plays in this transport of electricity through a solution, and he made a careful study of the concentration changes that occur within the immediate vicinity of the electrodes during electrolysis. Smith† has explained these changes in the following admirable manner.

Consider the electrolysis of a binary electrolyte, MX , which, in solution, yields ions of the same valency, and let O and K , Fig. 14, represent parts of the anode and kathode, respectively,

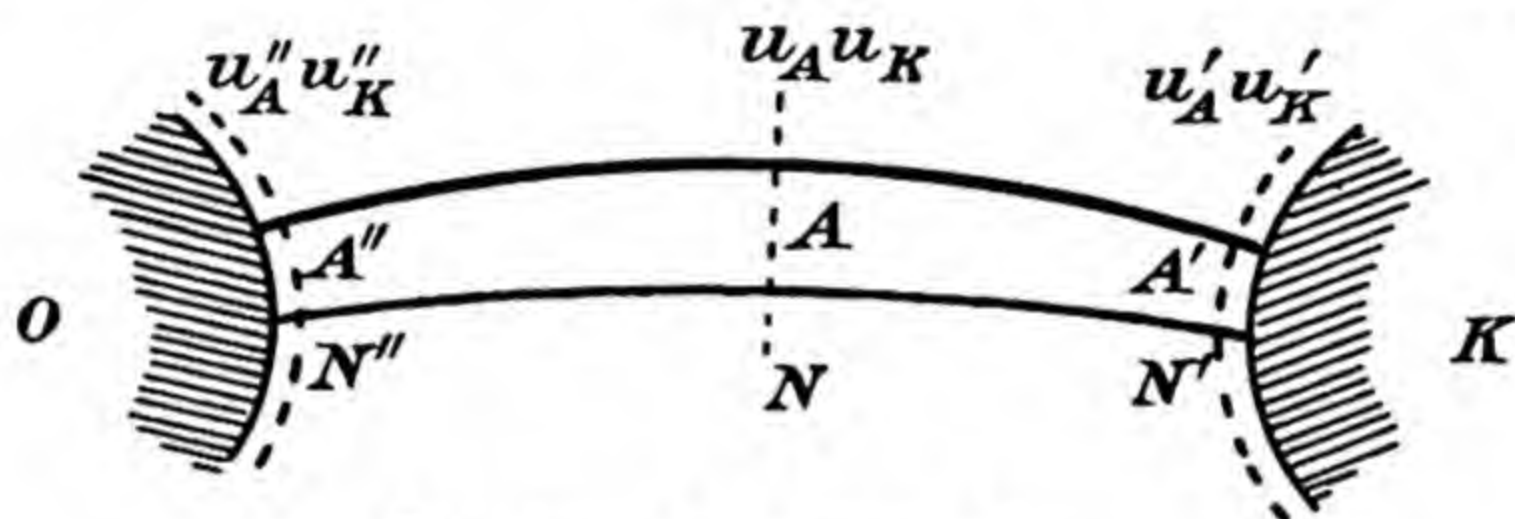


FIG. 14.—Migration of ions.

the curves extending between them representing the section of solution bounded by current stream lines, *i.e.*, lines along which the current is supposed to flow. Then the electric current passing across any section, perpendicular to the tube, must be the same at all such sections, otherwise there would be an accumulation of free electricity in different parts of the tube. Let A be *any* cross-section of the tube, A' and A'' being cross-sections very close to the electrodes. Suppose the potential gradients within the tube are such that u_A and u_K are the ionic velocities, respectively, and N , the number of gram ions of each kind per unit volume near A . Let u_A' , u_K' and N' , and u_A'' , u_K'' , N'' , be the corresponding quantities for the sections A' and A'' , respectively. In order that there shall be no accumulation of free electricity at any part of the tube we must have

$$ANF(u_A + u_K) = A'N'F(u_A' + u_K') = A''N''F(u_A'' + u_K''),$$

* *Pogg. Ann.*, 89, 177 (1853).

† *Proc. Phys. Soc.*, 28, 148 (1916).

where F is the charge carried by a gram univalent ion. Assuming that the ionic velocity is proportional to the potential gradient,

$$\frac{u_A}{u_K} = \frac{u_A'}{u_K'} = \frac{u_A''}{u_K''},$$

and, therefore, $ANu_A = A'N'u_A' = A''N''u_A''$.

Also, $ANu_K = A'N'u_K' = A''N''u_K''$.

Since the current flowing across any section of the tube is

$$AN(u_A + u_K)F,$$

the number of gram kations deposited on the kathode must be

$$AN(u_A + u_K) = A'N'(u_A' + u_K'),$$

and similarly the number of gram anions deposited upon the anode is

$$AN(u_A + u_K) = A''N''(u_A'' + u_K'').$$

But the number of gram kations brought up to the kathode per second by migration, *i.e.*, by virtue of the current, is $A'N'u_K'$, and therefore $A'N'u_A'$ gram kations must appear in some other way. In addition, at the section A' , there must migrate towards the anode $A'N'u_A'$ gram anions per second. Thus the net result is that $A'N'u_A'$ gram kations and $A'N'u_A'$ gram anions must be found. They are taken from the $A'N'u_A'$ moles of salt that are present in the vicinity of the kathode. In other words, $A'N'u_A'$ moles of the solute, dissociating into their constituent ions, supply the necessary ions, and hence there is a loss in concentration around the kathode of $A'N'u_A'$ or ANu_A moles per second.

In a similar manner, within the neighbourhood of A'' there is a loss of concentration of the solute equal to ANu_K moles per second; of these, $ANu_K = A''N''u_K''$ gram anions are liberated at the anode, and $ANu_K = A''N''u_K''$ gram kations migrate towards the kathode. These results are practically self evident from Fig. 14. Hence we see that

$$\frac{\text{loss in concentration of solute round kathode}}{\text{loss in concentration of solute round anode}} = \frac{u_A}{u_K} \quad (69)$$

and the ratio $\frac{\text{kathode loss}}{\text{anode loss}}$ would, if measured, give the ratio of the ionic velocities.

It must be emphasised that these reductions in the concentration of the electrolyte occur when insoluble electrodes are used, or rather, when the metallic radical of the solute is different from that constituting either of the electrodes, *e.g.*, in the electrolysis,

of copper sulphate solution between platinum electrodes. If the anode material and the metallic ion in the electrolyte are both of the same metal, for example, a silver anode dipping into a silver nitrate solution, the result is different. The silver anode loses weight equal to the weight of silver deposited upon the kathode, so that, while $AN(u_A + u_K)$ gram kations are being deposited upon the kathode, the same number of kations leave the anode. Of these, ANu_K migrate to the kathode, and ANu_A remain within the vicinity of the anode. In addition, ANu_A gram anions enter the neighbourhood of the anode, and thus ANu_A moles of silver nitrate accumulate per second in this vicinity. Therefore, there is a gain in concentration of the solute around the anode equal to ANu_A , and a corresponding loss in concentration around the kathode. The concentration of the solution as a whole remains unaltered, the anode gain being counterbalanced by the kathode loss. In this case the current is carried from the anode to the solution by metallic ions only, just as it is from the solution to the kathode.

During the electrolysis of a silver nitrate solution between silver electrodes, the weight of silver ions deposited upon unit area of the kathode, per second, will be $N(u_A + u_K)$ gram ions, and the weight of metal contained in the salt molecules carried away from the kathode space in the same time is Nu_A . Hence we have the important relation

$$\frac{\text{weight of metallic ion lost around kathode}}{\text{weight of metallic ion deposited on kathode}} = \frac{u_A}{u_A + u_K}, \quad (70)$$

where $\frac{u_A}{u_A + u_K} = n_A$ is the transference number for the anion.

Instead of determining the weight of metallic ion lost around the kathode, the equal gain around the anode can be determined. An experiment conducted along these lines will give the transference numbers of the ions. In practice, it is not necessary experimentally to measure the weight of metallic ion deposited upon the kathode, since another voltameter may be placed in series with the experimental one, and, knowing the weight of metal deposited in the former during an experiment, the amount of metal deposited upon the kathode in the experimental vessel may be determined from the values of the electrochemical equivalents of the various metals.

47. Experimental determination of transference numbers.—The apparatus required to determine the ionic transference numbers of an electrolyte varies somewhat according

to the case studied, the concentration of the solution and the presence, or absence, of precipitation, or of gaseous products, at the electrodes ; but, in general, it is simply necessary to remove portions of the solution from the immediate neighbourhood of the electrodes, and to determine the concentration changes produced by the passage of a known quantity of electricity. The electrolysis, however, must be interrupted before the concentration changes reach the central portion of the solution. Many forms

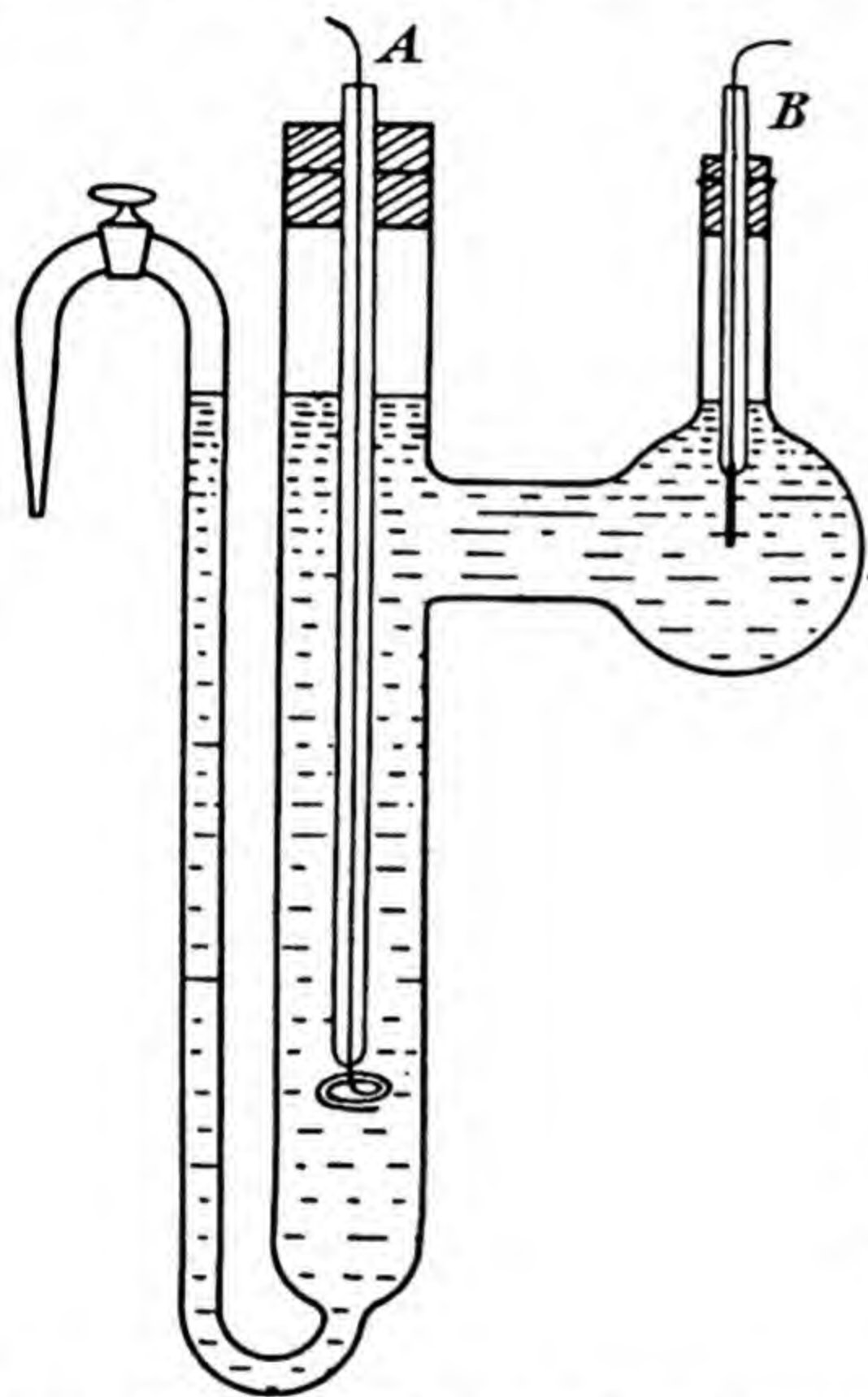


FIG. 15.—Determination of transference numbers by Hittorf's method.

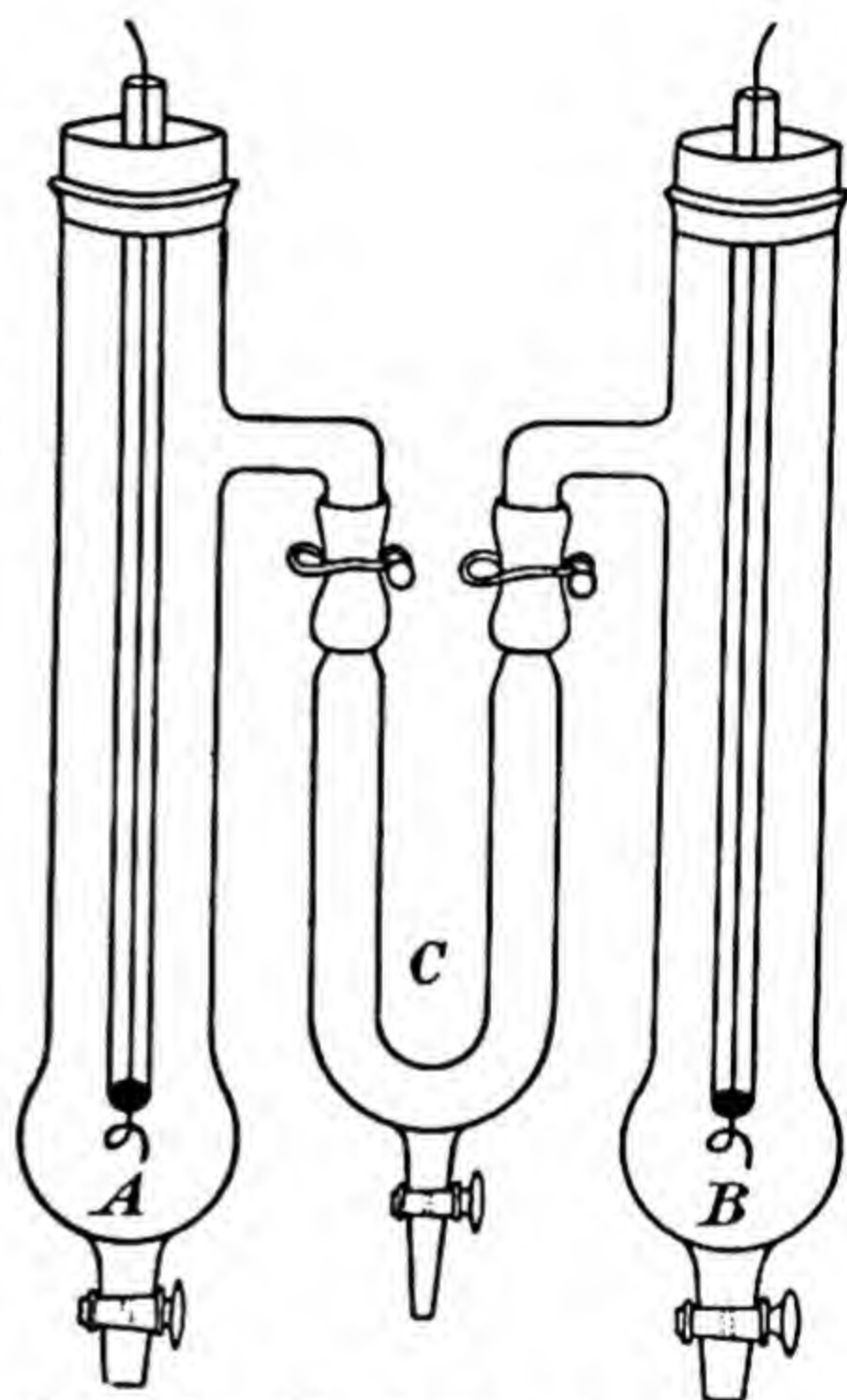


FIG. 16.—Findlay's apparatus for measuring transference numbers.

of apparatus have been adopted, but they all follow, in principle, that used by Nernst and Loeb * in their experiments on silver salts, shown in Fig. 15. The silver wire anode, A, is insulated for the greater part of its length by means of a glass tube, and opens out into a flat spiral at its lower end. The cathode B consists of a cylindrical sheet of silver foil, enclosed in a small side bulb, so that fragments of silver which fail to adhere to it during electrolysis may not fall on to the anode and disturb the

* *Zeits. phys. Chem.*, 2, 948 (1888).

results. The apparatus is filled with silver nitrate solution, and, as the solution near the anode becomes denser during the experiment and less dense around the kathode, convection currents arise. Disturbances due to these effects are avoided by placing the kathode at a higher level than that of the anode. The electrolytic cell is placed in series with a voltameter and a small current sent round the circuit. On account of the long column of electrolyte used in migration experiments, the resistance of the solution is high, and a fairly large voltage is required. At the conclusion of the experiment, liquid near the anode is removed, and its total salt content determined. A second portion of the solution, which represents the central part of the solution, and which should remain unchanged in concentration during the experiment, is drawn off and its salt content measured. The first portion of solution removed must consist of so much of the liquid near the anode as to contain all of the salt increase which the current has produced.

Another example of the many types of apparatus, suitable for determining the transference numbers, is that designed by Findlay,* and shown in Fig. 16. The middle portion of the solution is easily separated at the end of the experiment. Three tubes A, B, C are furnished with stop-cocks by means of which the solution can be run out. The two outer tubes are connected to the U-tube with rubber tubing, furnished with spring clips. These are kept open during an experiment, but are closed after the experiment is finished, and the solution for analysis is run through the stop-cock at the bottom of the appropriate outer tube. Some of the liquid in the U-tube, representing that in the middle section, is also collected. The apparatus is simple to use, and may be employed with most solutions if gases are not evolved during the electrolysis.

The method used in calculating the transference numbers from experimental data is illustrated by the following example:—

Consider a silver nitrate solution, the original strength of which is 1.1000 grams of silver nitrate per 100 grams of aqueous solution. Electrolysis then proceeds, and in a copper voltameter, placed in the circuit, it is found at the end of the experiment that 0.0227 gram of copper has been deposited. The final strength of the silver nitrate solution around the anode is 0.3999 gram of salt per 30.5403 grams of solution. Thus, after electrolysis, 0.3999 gram of silver nitrate is associated with 30.1404 grams of water, and originally this amount of water contained 0.3352 gram of

* *Chemical News*, 100, 185 (1909).

the salt. Hence the increase in the weight of salt around the anode is 0.0647 gram, and so the gain in the amount of silver ions in this part of the solution is 0.0410 gram. Since the weight of copper liberated is 0.0227 gram, the weight of silver deposited upon the kathode in the experimental cell is 0.0771 gram, and from equation (70),

$$n_A = \frac{u_A}{u_A + u_K} = \frac{0.0410}{0.0771} = 0.532,$$

from which it follows immediately that the transference number of the kation, Ag^+ , is

$$n_K = 1 - n_A = 0.468.$$

48. Change of transference number with concentration and temperature.—In general, the transference numbers depend upon the concentration of the solution, but in most cases this dependence does not become pronounced, until concentrations are reached at which the viscosity of the solvent is materially affected by the presence of the electrolyte. As the ionic velocity in a solvent depends upon the viscosity, we may infer that the variation in the transference number at the higher concentrations is due, in part at least, to the changing viscosity of the solution. The transference numbers for uni-univalent substances at 18° C. do not vary more than 3×10^{-3} units throughout the concentrations range 0.005 — 0.1 normal, except for nitric acid and lithium chloride, but for the halides and sulphates of the bivalent metals and for lithium chloride they decrease steadily and rapidly with increasing concentration. This large change is probably due, not to physical causes, but to changes in the composition of the ions. The transference numbers of uni-bivalent salts, unlike those of the bivalent halides, show little, if any, change with concentration, which fact suggests that intermediate ions, such as KSO_4^- or NO_3Ba^+ , and complex ions such as $\text{K}_2(\text{SO}_4)_2^{--}$, are not present in large quantities in solutions of these salts at concentrations below 0.2 normal.

The transference numbers for hydrochloric acid and sulphuric acid are practically constant within the concentration range 0.005 — 0.1 normal, but they differ from those calculated for these solutions at infinite dilution. The numbers for the bivalent halides and sulphates vary considerably with concentration above 0.1 normal, and for cadmium in cadmium iodide solutions, at and above 0.5 normal, they are actually negative. These effects are attributed to complex ions present in the solutions.

The transference numbers of both ions in potassium chloride are, approximately, 0.5 and therefore each ion carries practically one half of the current, so we assume that the chlorine and potassium ions are of the same size.

As the temperature increases, the transference numbers for all electrolytes approach the value 0.5, and the ionic mobilities tend towards the same value. This result applies to all combinations of positive and negative ions and therefore, if various salts contain similar negative ions, but different positive ones, it is evident that, provided the degree of dissociation remains the same in all cases, the equivalent conductance of these salts must approach a common value as the temperature increases. From this it follows that the smaller the equivalent conductance of an elec-

TABLE XXVII.

INFLUENCE OF TEMPERATURE AND CONCENTRATION ON THE TRANSFERENCE NUMBERS OF KATIONS.

Electro-lyte.	Tem-perature C.	Kation Transference Number at Concentration							
		0.005 N.	0.01 N.	0.02 N.	0.05 N.	0.1 N.	0.2 N.	0.5 N.	1 N.
NaCl	0	.387	.387	.387	.386	.385	—	—	—
	18	.396	.396	.396	.395	.393	.390	.382	.369
	30	.404	.404	.404	.404	.403	—	—	—
	96	—	—	—	.442	.442	.442	—	—
KCl	0	.493	.493	.493	.493	.492	.491	—	—
	10	—	.495	.495	.495	.495	—	—	—
	18	.496	.496	.496	.496	.495	.494	—	—
	30	.498	.498	.498	.498	.497	.496	—	—
LiCl	18	—	.332	.328	.320	.313	.304	—	—
NH ₄ Cl	18	—	.492	.492	.492	—	—	—	—
AgNO ₃	30	—	.495	.495	—	—	—	—	—
	18	—	.471	.471	.471	.471	—	—	—
HCl	25	—	.477	.477	.477	—	—	—	—
	0	.847	.846	.844	.839	.834	—	—	—
	10	.840	.840	.841	—	—	—	—	—
	18	.832	.833	.833	.834	.835	.837	.840	.844
BaCl ₂	30	—	.822	.822	.822	—	—	—	—
	0	.439	.437	.432	—	—	—	—	—
	25*	.441	.438	—	.425	.416	.379	.379	.353
	30	.445	.444	.443	—	—	—	—	—
CdBr ₂	18	.430	.430	.430	.430	.429	.410	.350	.222
CdI ₂	18	.445	.444	.442	.396	.296	.127	.003	—
K ₂ SO ₄	18	—	.494	.492	.490	—	—	—	—
H ₂ SO ₄	20	—	—	.822	.822	.822	.820	.816	.812
MgSO ₄	32	—	—	.808	.808	.808	—	—	—
	18	.388	.385	.381	.373	—	—	—	—
CdSO ₄	18	—	.389	.384	.374	.364	.350	.323	.294
CuSO ₄	18	—	—	.375	.375	.373	.361	.327	—

* See Jones and Dole, *Jour. Amer. Chem. Soc.*, 51, 1073 (1929).

trolyte, the greater is its temperature coefficient. Such a result holds experimentally, not only for very weak solutions, but also at moderate dilutions.

Values of the transference numbers for different kations in solutions at various concentrations and temperatures are given in Table XXVII.* It will be observed that for potassium chloride the number varies only slightly with temperature, whereas for sodium chloride it increases considerably as the temperature is raised.

49. Solvation of the ions.—In considering the transference numbers we have assumed, so far, that the ions migrate through the solution, the water remaining stationary throughout the duration of the electrolysis. But the relation between equivalent conductance and viscosity does suggest that, in some cases at any rate, molecules of the solvent are attached to the ion and move along with it. We have referred to this phenomenon as hydration of the ions in the case of water, but the effect takes place in other solvents, so that a more general term—*solvation of the ions*—has been introduced.

A great deal of evidence has accumulated along various lines in favour of the view that ions are, more or less, solvated. Amongst the strongest evidence is that which has been deduced from the results of transference experiments, carried out with various salt solutions in the presence of different non-electrolytic reference substances. If, at the end of such an experiment, the ratio of solvent to non-electrolyte has changed at the electrodes, then it follows, either that the ions have carried solvent in the one direction, or that they have transported the non-electrolyte in the opposite direction. Buchböck,† who was the first to obtain satisfactory quantitative results by this method, electrolysed hydrochloric acid solutions, using mannite or resorcinol, at widely different concentrations, as the reference substance. Washburn ‡ added raffinose, which is optically active, and measured the optical rotation of the solution near the electrodes both before and after electrolysis had occurred. From his results he calculated the original and final concentrations of the raffinose, and determined the change in the amount of water at the electrodes.

All the experiments agreed, and unless we are prepared to assume that the different reference substances are capable of combining with the ions in the same way, the conclusion would

* See Noyes and Falk, *Jour. Amer. Chem. Soc.*, **33**, 1436 (1911).

† *Zeits. phys. Chem.*, **55**, 563 (1906).

‡ *Jour. Amer. Chem. Soc.*, **31**, 322 (1909); *Zeits. phys. Chem.*, **66**, 513 (1909).

seem to be justified that the change in the ratio of solvent to non-electrolyte at the electrodes must be due, at least in the main, to the transfer of solvent by the ions from one part of the solution to another.

The electrons of the molecules constituting the solvent remain attached to their respective molecules, and on applying an external electric force, the electrons and the residual positive charge tend to move in opposite directions. Although the actual state of affairs may be complicated in any case, we shall have, on the whole, positive electricity at one end of the molecule and negative electricity at the other, and in this state the molecule is said to be *polarised*. A positive and an equal negative charge, situated at a small distance apart in this manner, form an *electric doublet* or *dipole*. In general, therefore, ions will polarise the molecules of a solvent in which they are situated, and any particular ion will be surrounded by oriented polarised solvent molecules, held, more or less firmly, to an extent which depends upon their distance from the ion. Hence when the latter moves under the influence of an external electric field, we should expect the ion to carry with it a sphere or sheath of the solvent.*

Closely related to this phenomenon is the *salting out* process. Consider, for example, a solution of ether in water. Upon dissolving an electrolyte in the mixed solvents, the water and ether molecules distribute themselves around the ions, this distribution depending upon the distance from an ion. There will be a relatively greater concentration of the more highly polarisable water molecules, the ether molecules being expelled to some distance from the ion. This is an example of the salting out phenomenon. The hydrogen ion is unique in that it consists of a single proton, probably combined with one water molecule to form a H_3O^+ ion. The hydrogen ion is thus hydrated, and is apparently buried within a water molecule. The other so-called hydrated ions are surrounded by oriented water molecules which the ions carry with them as they move.

It is evident, therefore, that the radius, b , of an ion, as determined with the aid of Stokes's law, is greater than the radius b_0 , of the ion proper, and the space occupied by the solvation envelope is obtained by deducting the molecular volume of the ionic body

* In the case of an anion these water molecules will be oriented with the hydrogen inwards, while those around the kation will be oriented with the oxygen inwards. The oriented molecules are strongly attracted to the central pole and will tend to squeeze out any non-polar molecules from its immediate neighbourhood. The attraction of the water molecules to the ions will also tend to drive the ions apart, since in this way they will be able to hold a larger quantity of water than when acting as ionic doublets in concentrated solutions.

proper from the ionic volume as calculated by means of Stokes's law. If this result is divided by the molecular volume of a solvent molecule the actual number of solvent molecules within the envelope is determined. It should be noted, however, that owing to the strong ionic forces existing within the solution, the packing of the molecules in the envelope will be much denser than in the free solvent. Ulich * has calculated some solvation numbers in this manner. His results are shown in Table XXVIII. :—

TABLE XXVIII.
SOLVATION NUMBERS.

Solvent.	Solvation Number.					
	Li ⁺ .	Na ⁺ .	K ⁺ .	Cl ⁻ .	Br ⁻ .	I ⁻ .
Water	6-7	2-4	—	—	—	—
Methyl alcohol	7	5-6	4	4	2-4	0-3
Ethyl alcohol	6	4-5	3-4	4-5	4	2-3
Acetone	4	4-5	4	2	1	0-1
Acetonitrile	—	5	3-4	—	1-3	0-2
Furfural	—	5	4	—	—	0-1
Pyridine	—	4	2-3	—	—	0-1

The solvation of the kations appears to be fairly constant for all solvents, whilst that of the anions is decidedly smaller in acetone, furfural and pyridine than in the alcohols. The iodide ion seems to have a very small, if any, fixed solvation envelope, in these solvents.

If N_s^A and N_s^K represent the number of moles of solvent associated with each gram anion and gram kation, respectively, and n_A , n_K , the transference numbers in the absence of solvation, then the net electrolytic transference, N_s , of the solvent per faraday, is given by

$$N_s = n_K N_s^K - n_A N_s^A. \quad . \quad . \quad . \quad (71)$$

Various investigators † have shown that organic ions in water, at any rate the larger ions, do not carry any water envelopes, so that it should be possible to determine the absolute value of the water carried by an inorganic ion in cases when the other ion is organic since one of the terms of the right-hand side of

* *Trans. Farad. Soc.*, 23, 392 (1927).

† Hevesy, *Jahrl. f. Radioakt und Elektromek*, 11, 419 (1914); 13, 271 (1916); Lorenz, *Zeits. anorg. Chem.*, 94, 240 (1916).

equation (71) vanishes. Thus Remy and Reisener* found that if the electrolyte contained an organic kation, the direction of water transport was, in normal solutions, in the opposite direction to that of the electric current. In other words, the organic ion carried little, if any, water. These experimenters measured the water transport of aniline hydrochloride, and the value obtained represents the water carried by the chloride ion. Knowing the true transference numbers of this salt, they calculated N_s^A , the number of water molecules in the envelope surrounding the chloride ion, to be three. From this value they then determined the degree of solvation of other inorganic ions. Measurements were made, using chlorides, bromides and iodides, the hydration numbers of the chloride, bromide and iodide ions being 3, 2.1 and 3.7, respectively. From the results, shown below, it will be seen that there is fair agreement between the values as determined from the three solutions. The numbers quoted refer to the number of water molecules carried by each ion in *normal* solutions:—

HYDRATION OF THE IONS.

Ion.	Number of Water Molecules Carried with each Ion in Solution.		
	Chlorides.	Bromides.	Iodides.
H ⁺	0.9	1.1	—
Li ⁺	12.6	—	—
Na ⁺	7.4	8.8	—
K ⁺	4.1	4.0	—
Cs ⁺	3.8	—	—
NH ₄ ⁺	4.4	—	—
NH ₃ OH ⁺	2.8	—	—
Mg ⁺⁺	14.1	11.9	11.7
Ca ⁺⁺	12.1	8.1	8.7
Sr ⁺⁺	7.7	7.7	9.5
Ba ⁺⁺	4.5	3.1	(7.8)

Baborovsky and Wagner,† using aqueous hydrobromic acid solutions, found that the hydration of the hydrogen ion was 0.50 in normal solutions and that the bromide ion travels with 3.08 molecules of water. Baborovsky ‡ also studied the electrolytic transference of water in solutions of the chlorides of sodium, potassium and lithium, and also in hydrochloric acid, at concentrations from normal to 0.1 normal. In addition, he worked with the bromides of the three metals in normal solutions. He

* *Zeits. phys. Chem.*, 126, 161 (1927).

† *Ibid.*, 131, 129 (1928).

‡ *Ibid.*, 129, 129 (1927).

calculated that the ions take up the following numbers of water molecules :—

H ⁺	K ⁺	Na ⁺	Li ⁺	Cl ⁻	Br ⁻
2	5	8-9	13-14	4	3

It will be noted that if the alkali metal kations are arranged in order of diminishing hydration, the caesium ion occupies the lowest position, and whereas Ulich * calculated for the lithium ion a hydration number of 6, Remy † deduced 12.6 as the value, but Remy's figure holds for a normal solution, and Ulich's for infinite dilution. On the other hand, Riesenfeld ‡ has calculated the water sheath of the lithium ion to be 158 molecules at infinite dilution. The reason for the discrepancy between Ulich's and Remy's hydration numbers for the sodium and lithium ions seems to be that trustworthy calculations are not possible by Ulich's method, since the true volume of the solvent molecule attached to the ions is unknown. In addition, it is possible that, from the nature of the experimental methods, Remy's figures for water sheaths not only took into account the true closely bound water molecules, but also included, to some extent, the water circulating around the ion. This would explain Remy's higher values.

Lindemann § has developed a theory which leads to the view that the ions are not hydrated in the sense that water molecules are combined with the ion, travelling as a quasi-rigid entity, but that the ions tend to transfer momentum to the solvent, thus causing transference of the solvent in the direction they are travelling, and giving rise to the phenomena usually ascribed to hydration. The lighter ions, such as lithium, will transfer more momentum than the heavier ones. Wessel || suggested that the ions in the interior of a solution are, through hydration, surrounded by a mobile envelope of water molecules of a thickness of several molecular radii, the molecules being grouped in accordance with their bipolar nature. On reaching the surface a partial dehydration of the ions occurs since the complete water envelope can now only occur on the solution side of the ion. Large ions are more easily dehydrated and brought to the surface than smaller ones.

50. True transference numbers.—Since ions are solvated, a transfer of water takes place from one electrode to the other when the ions move through water. Unless the number of water molecules carried by each ion is the same, there will be,

* *Trans. Farad. Soc.*, 23, 392 (1927).
 † *Zeits. phys. Chem.*, 66, 672 (1909).
 || *Ann. d. Phys.*, 77, 21 (1925).

† *Ibid.*, 23, 387 (1927).
 § *Ibid.*, 110, 394 (1924).

on the whole, a net movement of water within the solution. If this is so, the measured changes of ionic concentrations, which occur at the electrodes during electrolysis, will not entirely represent variations in the number of ions brought about by migration, and under these circumstances the transference numbers, as determined by means of the method described in **section (47)**, are not the true values. This water transference may be measured experimentally by introducing into the solution a substance which is electrolytically inactive. The change in the concentration of the salt with respect to this reference substance gives the true transference number, and the relation between the true and "Hittorf" transference numbers is obtained from the equations,

$$n_K = n_K + CN_w, \quad . \quad . \quad . \quad (72)$$

and
$$n_A = n_A - CN_w, \quad . \quad . \quad . \quad (73)$$

where N_w indicates the electrolytic transference of water, per faraday, n_K and n_A , the true transference numbers, respectively, n_K and n_A , the experimental Hittorf transference numbers, respectively, and the electrolyte concentration C is expressed in equivalents per mole of water. Washburn,* by means of transference experiments in the presence of raffinose, determined the true transference numbers for a series of electrolytes, and obtained for the kations the following values :—

Electrolyte (1.3 normal)	HCl	CsCl	KCl	NaCl	LiCl
Values of n_K	0.844	0.491	0.495	0.383	0.304

In these solutions the net water transference takes place from the anode to the kathode, and the relation between the number of water molecules carried by the kation and chloride ion, respectively, is given by the equations,

$$N_w^H = 0.28 \pm 0.04 + 1.085N_w^{Cl}.$$

$$N_w^{Cs} = 0.67 \pm 0.1 + 1.03N_w^{Cl}.$$

$$N_w^K = 1.3 \pm 0.2 + 1.02N_w^{Cl}.$$

$$N_w^{Na} = 2.0 \pm 0.2 + 1.61N_w^{Cl}.$$

$$N_w^{Li} = 4.7 \pm 0.4 + 2.29N_w^{Cl}.$$

The number of water molecules transported by the chloride ion being three, the absolute hydration of the kations may be calculated by means of these equations.

Remy † used a diaphragm method to measure this water electrolytic transference. Originally he employed a gelatine diaphragm, but afterwards substituted one of parchment. His

* *Jour. Amer. Chem. Soc.*, 31, 322 (1909).

† *Trans. Farad. Soc.*, 23, 383 (1927).

results are given together with others in Table XXIX. which also includes the anion transference numbers, at infinite dilution, calculated from Kohlrausch's values of the ionic mobilities.

TABLE XXIX.

TRUE TRANSFERENCE NUMBERS FOR INORGANIC ELECTROLYTES (NORMAL AQUEOUS SOLUTIONS).

Electrolyte.	Water Transference.	Hittorf Transference Number.	True Transference Number.	Transference Number at Infinite Dilution.
HCl	.28	.156	.151	.172
LiCl	.37	.156	.149	
"	1.5	.739	.711	.662
"	1.4	.739	.713	
NaCl	1.6	.739	.710	.601
"	.81	.637	.622	
"	.82	.637	.622	
"	.85	.637	.621	
"	1.0	.637	.619	.503
KCl	1.4	.637	.611	
"	.60	.514	.503	.504
"	.57	.514	.503	
"	.47	.514	.505	.491
"	.47	.514	.505	
CsCl	.36	.515	.509	.506
NH ₄ Cl	.55	.514	.504	
"	.87	.514	.498	.593
$\frac{1}{2}$ MgCl ₂	— .08	.709	.710	
$\frac{1}{2}$ CaCl ₂	— .20	.686	.690	.562
$\frac{1}{2}$ SrCl ₂	— .97	.686	.704	.562
$\frac{1}{2}$ BaCl ₂	— 1.23	.640	.663	.544
HBr	.61	.164	.153	.177
NaBr	2.2	.642	.601	.608
KBr	.84	.532	.516	.511
$\frac{1}{2}$ MgBr ₂	.30	.709	.704	.600
$\frac{1}{2}$ CaBr ₂	— .17	.684	.687	.570
$\frac{1}{2}$ SrBr ₂	— .24	.684	.688	.570
$\frac{1}{2}$ BaBr ₂	— .84	.643	.659	.551
$\frac{1}{2}$ MgI ₂	— .67	.670	.682	.578
$\frac{1}{2}$ CaI ₂	— .92	.637	.654	.566
$\frac{1}{2}$ SrI ₂	— .75	.636	.650	.566

From these results we see that the true transference number for potassium chloride agrees with its value at infinite dilution. For other salts of the same type, the "Hittorf transference numbers" are greater than the true ones, and the latter, greater than those for infinitely dilute solutions. The true transference numbers for the halogen hydrides and for the halides of the alkaline earth metals, except magnesium bromide, differ more markedly among themselves than the experimentally determined numbers.

51. True mobilities.—Since the Hittorf transference numbers differ from the true transference numbers it is evident that in using equation (47) the true transference number n_K should be employed where

$$U = n_K \Lambda, \quad (74)$$

U being termed the *true mobility* of the kation, in analogy to the true transference number. By combining equations (72), (73) and (74), we obtain

$$\begin{aligned} U &= U + CN_w \Lambda, \\ V &= V - CN_w \Lambda, \end{aligned} \quad (75)$$

U and V being the uncorrected values of the mobilities or conductances. The true mobility of an ion is independent of the method of measurement, but its value is much influenced, as is that of the apparent mobility, by the nature of the ion with which it is associated.

If we compare two electrolytes having a common ion, the "non common" ions being halogens, and determine the product of the mobility and the viscosity coefficient, η , the values so obtained agree better among themselves when the true mobility values are used in the calculation, than when the values employed are those of the apparent mobilities. This is illustrated by the results shown in Table XXX.*

TABLE XXX.

APPARENT AND TRUE IONIC MOBILITIES IN NORMAL SOLUTIONS.

Electrolyte.	Λ .	η .	U .	U .	$U\eta$.	$U\eta$.
		18° C.				
KCl	98.3	.01055	50.53	49.54	.533	.523
NaCl	74.3	.0116	47.33	45.99	.549	.533
KBr	100.6	.01031	53.52	51.91	.552	.535
NaBr	78.1	.01145	50.14	46.94	.574	.537
		20° C.				
KCl	98.3	.010095	50.53	49.54	.510	.500
NaCl	74.3	.011225	47.33	45.99	.531	.516
BaCl ₂	70.1	.013156	44.86	46.48	.590	.611
CaCl ₂	67.5	.013320	46.31	46.58	.617	.620
MgCl ₂	61.5	.013503	43.60	43.67	.589	.590

52. Moving boundary method of determining transference numbers.—There is a second method available for measuring the transference numbers, the actual rate of motion

* See Remy, *Trans. Farad. Soc.*, 23, 384 (1927).

of the ions being observed as they move along, under the influence of an applied potential difference. Lodge,* who was the first directly to measure the movement of an ion, made the invisible ion indicate its presence by some characteristic physical or chemical property. A horizontal glass tube, connecting two vessels filled with dilute sulphuric acid, contained a solution of sodium chloride in solid agar-agar jelly. The latter eliminated disturbance in the solution, made alkaline by means of a trace of caustic soda, to bring out the red colour of a little phenol phthalein. When an electric current was passed through the tube, the hydrogen ions from the anode vessel of acid moved along the tube and decolorised the phenol phthalein. Lodge's results gave an average value for the velocity of the hydrogen ion of 0.0026 cm. per second per volt-cm.

In other experiments, the point at which two ions, travelling from opposite ends of the same tube, formed a precipitate, was considered to divide the tube in the ratio of the respective velocities of the two ions. Of the various values obtained, only that of the hydrogen ion was in agreement with those measured by Kohlrausch, the difference being due to a faulty assumption regarding the distribution of potential in the circuit.

Whetham† used a method which rendered the jelly unnecessary, as he avoided gravity, or convection, currents by employing a vertical tube in which to observe the rate of movement of the boundary between coloured and colourless solutions during the passage of a current, the less dense solution lying above. He also avoided different and unknown potential gradients in different parts of the column by selecting, for each experiment, a pair of solutions of as nearly as possible equal specific resistances. In addition the solutions had one ion in common.

In all of these experiments the definiteness and sharpness of the solution junction depends upon the relative conductivities of the solutions. The potential gradients within the solutions will be proportional to their specific resistances, and if one ion, say the anion, is common, the solution of higher resistance will be the one in which the kation has the lower relative velocity. Hence when a current is passed from the liquid of higher to that of lower specific resistance, any kation, which happens to move in front of the boundary, enters a region of smaller potential gradient, and is at once retarded, being brought back into line. Similarly, if a fast moving ion in the solution of lower specific resistance lags behind the moving boundary, it comes within the higher

* B.A. Reports, 389 (1886).

† *Phil. Trans.*, A, 184, 340 (1893).

potential gradient region and is at once accelerated. In this manner the boundary is maintained sharp and distinct, and therefore, as pointed out by Kohlrausch * and Weber,† the necessary condition for the existence and permanency of a sharp boundary is that the specifically slower moving ion shall follow one of greater velocity.

Masson ‡ used a horizontal tube T, Fig. 17, filled with molten jelly which was allowed to set at experimental temperature, the jelly containing a known quantity per c.c. of salt, KCl, whose ionic velocities it was desired to measure. Suitable solutions, such as copper sulphate in the anode vessel A, and potassium chromate in B, were employed, and the visible moving boundaries marked not only the rates of advance of the foremost copper and chromate ions, but also those of the rearmost potassium and chloride ions.

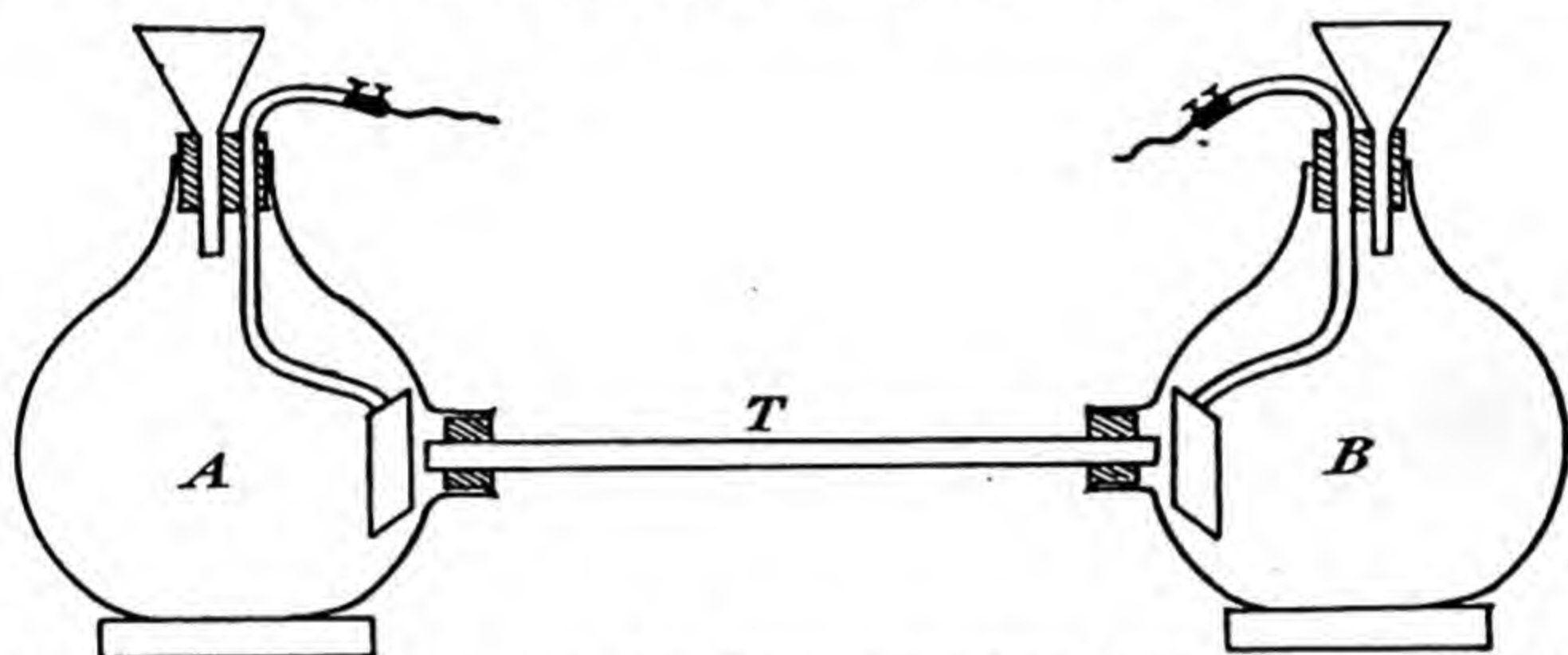


FIG. 17.—Masson's apparatus for determining transference numbers by the moving boundary method.

The latter themselves are invisible, but following immediately behind the coloured ions the latter may be taken as their indicators. The intermediate colourless part of the jelly is, at the start, of uniform composition, and remains so throughout the experiment, so that both the degree of ionisation of the potassium chloride, and the potential gradient within it, have constant values from start to finish in all parts of the colourless jelly. Therefore the rearmost potassium ions at one end, and the rearmost chloride ions at the other, are under similar conditions, and a comparison of their actual velocities, u_K and u_A , made visible by the indicators, gives at once the ratio $\frac{u_A}{u_K}$ for the particular concentration employed. This result may also be put in the form of the Hittorf

* *Wied. Ann.*, 62, 209 (1897).

† *Sitz. Akad. Wiss. Berlin*, 936 (1897).

‡ *Phil. Trans.*, A, 192, 331 (1899).

transference ratio, $\frac{u_A}{u_A + u_K}$. The observed values of the velocities are also those of the copper and chromate ions, but the experiment affords no indication that the potential gradients, under which these ions move, are the same. They are, in fact, very different. There is no intermingling of the ions at the blue and yellow boundaries, provided that the coloured ion is specifically slower moving than the one it follows. Imagine a naturally slow copper ion travelling behind a naturally faster potassium ion, with the chlorine ions travelling quickly in the opposite direction. If the copper ions lag behind the potassium ions, or the latter move away from the former, a region will be established where the kations are deficient, a state of affairs that must immediately correct itself by reason of the resulting potential gradient. If, on the other hand, they keep pace with one another, as in fact they do, it must be by virtue of a steeper potential slope in the blue. If now some K^+ ion accidentally lags behind its fellows, it will find itself in this region, and will be at once hurried forward again, while any Cu^+ ion trying to penetrate the "potassium" region will be forced to drop back. Masson's results for sodium, potassium, and ammonium salts give smaller values for the anion transference numbers than the smallest value obtained by Hittorf.

Denison and Steele* extended Masson's method in two directions, first by substituting aqueous for gelatine solutions, and secondly, by observing the boundary between two colourless solutions which is visible on account of the difference in the refractive indices of the two solutions. The method compares the velocities of the anion and kation, and therefore determines the ratio $\frac{u_A}{u_A + u_K}$. It also measures, in the case of salts like sodium chloride, the actual velocity $u_K = \alpha u_K$, where u_K is the observed velocity and α the coefficient of ionisation. As kation indicators these experimenters used, among others, normal solutions of the following salts, copper sulphate with a copper anode to minimise the formation of hydrogen ions, cadmium sulphate with cadmium anode, and potassium chloride containing dissolved potassium carbonate. The anion indicators included sodium acetate with acetic acid to minimise the formation of hydroxyl ions and potassium chromate with potassium bichromate. At frequent intervals the time, electric current, and distance traversed by the boundaries, were measured, and the ratio of the distances moved

* *Phil. Trans.*, A, 205, 449 (1906).

over by the two boundaries gave $\frac{u_A}{u_K}$, so that the value of $\frac{u_A}{u_A + u_K}$ could be determined immediately. Table XXXI. gives the

TABLE XXXI.

IONIC VELOCITIES BY MOVING BOUNDARY METHOD.

Salt.	Concentration.	Values of $u_K = \alpha u_K \times 10^4$. cms. per sec.		Values of $u_A = \alpha u_A \times 10^4$. cms. per sec.	
		Kohlrausch.	Denison and Steele.	Kohlrausch.	Denison and Steele.
KCl	0.02N	6.13	6.06	6.30	6.24
	0.5N	5.12	5.53	5.43	5.29
	2.0N	4.66	4.83	4.94	4.58
NaCl	0.1N	3.67	3.67	5.91	5.91
	1.0N	2.85	3.18	4.85	4.52
	2.0N	2.50	2.74	4.18	3.95
KBr	0.02N	6.11	5.98	6.29	6.42
	0.5N	5.42	5.68	5.53	5.16
	1.0N	5.22	5.42	5.32	4.84
BaCl ₂	2.0N	5.00	5.38	5.10	4.71
	0.02N	4.66	4.64	6.05	6.03
	0.5N	3.10	3.30	4.94	4.50
CuSO ₄	1.0N	2.64	2.83	4.65	4.57
	1.0N	.82	.80	1.86	1.55
	2.0N	.58	.55	1.50	1.51

values of these observed velocities, calculated from Kohlrausch's tables, and also those reduced from the authors' measurements.

The results show that the transference numbers for the simple alkali metal salts are practically independent of the concentration of the solution, but with other salts the general tendency is for the anion numbers to increase with concentration. In addition, Denison and Steele found that for a given dilution, the velocity of an ion depended upon the type of salt of which it formed a constituent, although with dilute solutions there was no such dependence.

Lewis* used an apparatus shown in Fig. 18 which was similar to that employed by Denison and Steele. The tube C was calibrated for three volumes between marks *a* and *a'*, *b* and *b'*, *c* and *c'*, the tube B acting as a trap to prevent the concentrated solution of lithium chloride, used in A, from reaching the measuring tube C. E and E were electrodes, and the glass rod R had a circular flat enlargement G tipped at its lower end with a cir-

* *Jour. Amer. Chem. Soc.*, 32, 862 (1910).

cular disc of rubber. D and C were filled with potassium chloride solution, and after some lithium chloride solution had been placed in the space above C and in the tube B, R was raised so that the boundary started moving down the tube. As the boundary passed each of the upper marks on the tube C, a voltmeter was connected in the circuit, and as the boundary crossed each of the lower marks, the corresponding voltmeter was disconnected from the circuit. In this way three independent measurements were obtained. The method of calculating the transference number is as follows:—

Let u_K' be the actual velocity with which the kation moves along and u_K its velocity under unit potential gradient. Then,

$$u_K' = u_K \frac{dE}{dl},$$

where $\frac{dE}{dl}$ is the potential gradient. Now the current, i , through the tube C (Fig. 18) is given by

$$i = (u_K + u_A) \frac{dE}{dl} \cdot CAF \cdot 10^{-3} = \sigma A \frac{dE}{dl},$$

where C is the concentration in gram equivalents per litre, A , the cross-sectional area in sq. cm. of the tube C and F , the faraday, σ , the specific conductance, being equal to

$$(u_K + u_A)CF \cdot 10^{-3}.$$

Then,

$$u_K = \frac{u_K' \sigma A}{i} = \frac{l \sigma A}{ti},$$

l being the distance traversed by the boundary in a time t .

Since

$$u_K' = u_K \frac{dE}{dl} = \frac{n_K \Lambda}{F} \frac{dE}{dl},$$

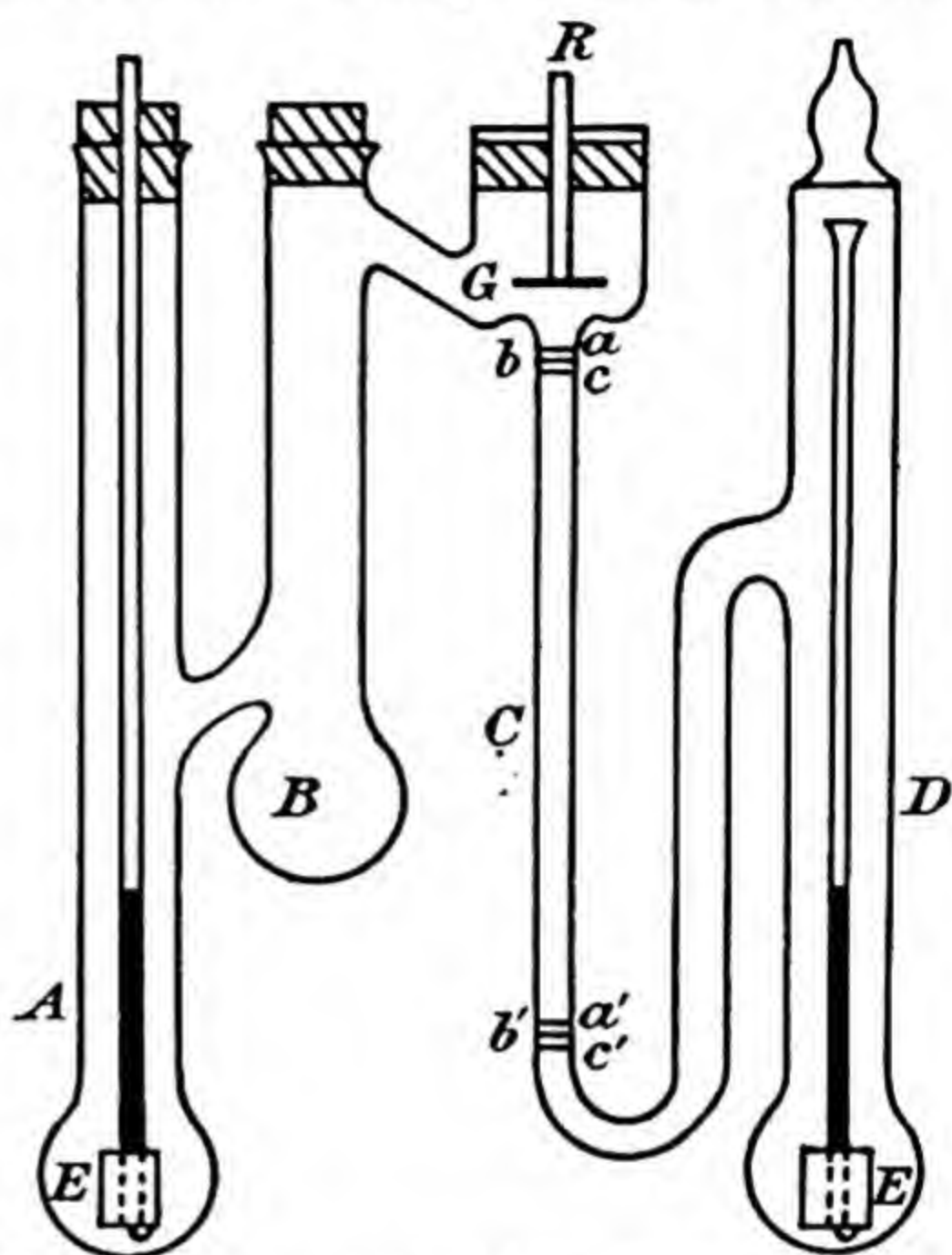


FIG. 18.—Apparatus for measuring transference numbers by the moving boundary method. (Lewis.)

and

$$\frac{dE}{dl} = \frac{i}{\sigma A}; \quad A = \frac{1000\sigma}{C},$$

$$n_K = \frac{u_K' CFA}{1000i} = \frac{lCFA}{1000ti} = \frac{vF}{v_0 Q},$$

where v is the volume passed through by the boundary, v_0 the volume of solution which contains one gram-equivalent of the salt, and Q the number of coulombs of electricity passing during the experiment.

Lewis has pointed out that it is necessary to correct the values, obtained for the transference numbers by the moving boundary method, for the flow of solution through the apparatus, caused by the volume changes occurring at the electrodes. He proves that

$$n_A^0 = n_A - C\delta v, \quad . \quad . \quad . \quad . \quad (76)$$

where n_A is the number obtained by the moving boundary experiment and n_A^0 that by the ordinary Hittorf method, δv being the volume changes produced when one faraday passes. The corrections for normal solutions of potassium chloride and of sodium chloride are 0.005 and 0.013, respectively. It is evident from equation (76) that as δv is nearly independent of concentration, the agreement between the transference numbers obtained by the "Hittorf" and moving boundary methods becomes closer as the dilution increases. This was verified by Denison and Steele.

Allowing for the correction δv ,

$$n_K = \frac{1}{v_0} \left(\frac{vF}{Q} \pm \delta v \right).$$

The moving boundary method only gives accurate results when

$$\frac{C}{n_K} = \frac{C'}{n_K'},$$

where C and n_K refer to the solution under observation, and C' , n_K' are the corresponding values for the indicator solution. Kohlrausch * quoted this relationship as a necessary condition for a stable moving boundary. The condition represented by this equation will be established automatically, if not present at the outset, so that the initial concentration of the indicator solution is of little importance. The correct value of n_K can be obtained from a series of experiments in which the conditions approach

* *Ann. d. Phys.*, 62, 209 (1897).

more and more closely to those demanded by Kohlrausch's relationship. If this adjustment is not made, the values are not entirely independent of the concentration of the indicator solution, or of the electric current through the apparatus. They may differ widely and erratically from the true values.

Table XXXII. gives a comparison of the kation transference numbers at 18° C. derived from the three methods, namely, gravimetric (G.), the moving boundary (M.B.), and conductance. It will be noted that the values obtained by means of the first two methods are concordant to within 1 per cent. for hydrochloric, nitric and sulphuric acids, potassium and ammonium chlorides, and for potassium sulphate. The values determined by the conductance method are about 1 to 3 per cent. higher than those calculated from the moving boundary experiments.

TABLE XXXII.

TRANSFERENCE NUMBERS DETERMINED BY DIFFERENT METHODS.

Salt.	Transference Numbers at Concentrations						Method.
	0 Conduct- ance method.	0.005 N.	0.02 N.	0.05 N.	0.10 N.	0.20 N.	
NaCl	.399	.396	.396	.395	.393	.390	G.
KCl	.496	.496	.496	.496	.495	.494	M.B.
NH ₄ Cl	.497	—	.493	—	.492	—	G.
NaBr	.391	.395	.395	—	.489	—	M.B.
KBr	.488	—	.495	.381	.376	—	G.
HCl	.828	.832	.833	—	.481	—	M.B.
CaCl ₂	.442	.438	.422	.834	.835	.837	G.
HNO ₃	.836	.839	.841	—	.835	—	M.B.
K ₂ SO ₄	.485	—	.492	.411	.402	.393	G.
H ₂ SO ₄	.821	—	.824	—	.398	—	M.B.
"	—	—	.833	.844	.855	—	G.
"	—	—	—	—	.485	—	M.B.
"	—	—	—	—	.824	.822	G.
"	—	—	—	—	.828	—	M.B.

It is possible to calculate the transference numbers, in cases where reliable experimental data are not available, in the following manner * :—

* See Remy, *Trans. Farad. Soc.*, 23, 381 (1927).

Since

$$V = n_A(U + V) = n_A\Lambda,$$

if we consider solutions of two electrolytes having a common kation, but chloride and bromide anions, respectively,

$$\frac{n_{\text{bromide}}^-}{n_{\text{chloride}}^-} = \frac{V_{\text{Br}^-}}{V_{\text{Cl}^-}} \cdot \frac{\Lambda_{\text{chloride solution}}}{\Lambda_{\text{bromide solution}}} \quad (77)$$

From Kohlrausch's table of ionic mobilities we have, at 18° C., the following ratios :—

Concentration	$\frac{V_{\text{Br}^-}}{V_{\text{Cl}^-}}$	$\frac{V_{\text{I}^-}}{V_{\text{Cl}^-}}$
0.0001N	1.032	1.011
0.001N	1.033	1.014
0.01N	1.036	1.019
0.1N	1.054	1.054

Accepting the value 1.054 as approximately correct for the ratio of the apparent mobility of the iodide to the chloride ion in normal solutions, and calculating the transference numbers of the iodides of the alkaline earth metals from those of the chlorides by means of equation (77), we have the following values for the iodide in different electrolytes :—

$$n_{\text{BaI}_2} = 0.611 ; n_{\text{CaI}_2} = 0.646 ; n_{\text{MgI}_2} = 0.670,$$

whereas the experimental values are,

$$n_{\text{BaI}_2} = 0.609 \pm 0.002 ; n_{\text{CaI}_2} = 0.637 \pm 0.002 ; n_{\text{MgI}_2} = 0.670 \pm 0.003,$$

respectively. The agreement is thus very good. In a similar manner the calculated values for the bromides are as follows :—

Salt	HBr	NaBr	KBr	$\frac{1}{2}\text{MgBr}_2$	$\frac{1}{2}\text{CaBr}_2$	$\frac{1}{2}\text{SrBr}_2$	$\frac{1}{2}\text{BaBr}_2$
n_A	0.164	0.642	0.532	0.709	0.684	0.684	0.643

53. Transference numbers in non-aqueous solvents.—

Many determinations of transference numbers in non-aqueous solvents have been made, but the experimental difficulties do not permit of accurate results, so that there is a lack of agreement in the values obtained by different observers. The relative velocities of most ions are practically the same in many solvents, but, as would be expected, the absolute velocities are quite different. Since by Walden's rule $\eta_0 U_0$ is constant and independent of the solvent, where η_0 is the viscosity of the solvent, and U_0 the mobility of an ion at infinite dilution, and if we assume Stokes's law to apply to the motion of the ions through solutions, *i.e.*, $u_A^0 \propto \frac{1}{\eta_0}$, it follows that $\frac{u_A^0 + u_K^0}{u_A^0}$ should be inde-

pendent of the nature of the solvent, where u_A^0 and u_K^0 are the velocities of the anion and kation, respectively, at infinite dilution. This relationship will not be true, however, if the ions are hydrated or associated to different degrees. It is evident, therefore, that the transference numbers in solvents may be calculated by means of Walden's rule. Thus, in methyl alcohol, the mean value found by Nonhebel and Hartley* for hydrochloric acid is $n_{H^+} = 0.735 \pm 0.005$, and Harned and Fleysher,† using solutions of the acid in ethyl alcohol, obtained the values 0.738 and 0.752, for the hydrogen transference number. Calculating ‡ by means of Walden's rule, the numbers for hydrochloric acid in these two solvents are $n_{H^+} = 0.733$ and 0.742, respectively. Thus there is close agreement between the values obtained by these different methods.

54. Transference numbers in mixed solutions. — Mackay§ measured the transference numbers for the chloride and sulphate ions in mixtures of potassium chloride and potassium sulphate, each of concentration 0.2009 normal. The transference number for the chloride ion in the mixture at 18° C. was found to be 0.289 ± 0.001 . The values for the sulphate ion were discordant (0.197 — 0.2217). Assuming that the relative mobilities of the Cl^- and K^+ ions are the same as in dilute potassium chloride solutions, the proportion of the current carried by the ions of potassium chloride in the mixture is 0.573, and by the ions of potassium sulphate, 0.3652, giving 0.02003 for the partial specific conductivity of potassium chloride in the mixture, and 0.01559 for the potassium sulphate.

The partial specific conductance of the potassium chloride thus determined is 2 per cent. greater, and that of the potassium sulphate 5.2 per cent. smaller, than the respective values calculated on the principle that each salt in the mixture has a degree of ionisation equal to that which it has when present alone in a solution, in which its ions have a concentration equivalent to that of the common ion in the mixture, the degree of ionisation being taken equal to the ratio $\frac{A\eta}{A_0\eta_0}$. In mixtures of potassium chloride and potassium sulphate, the transference numbers n_{Cl^-} and $n_{SO_4^{--}}$ are given by

$$n_{Cl^-} = \frac{C_{Cl^-} \cdot V_{Cl^-}}{C_{Cl^-} V_{Cl^-} + C_{SO_4^{--}} \cdot V_{SO_4^{--}} + C_{K^+} U_{K^+}},$$

* *Phil. Mag.*, 50, 729 (1925).

† *Jour. Amer. Chem. Soc.*, 47, 92 (1925).

‡ See Ulich, *Trans. Farad. Soc.*, 23, 389 (1927).

§ *Jour. Amer. Chem. Soc.*, 33, 308 (1911).

and
$$n_{\text{SO}_4^{--}} = \frac{C_{\text{SO}_4^{--}} \cdot V_{\text{SO}_4^{--}}}{C_{\text{Cl}^-} V_{\text{Cl}^-} + C_{\text{SO}_4^{--}} V_{\text{SO}_4^{--}} + C_{\text{K}^+} U_{\text{K}^+}},$$

where C_{Cl^-} , *etc.*, represent equivalent concentrations and V_{Cl^-} , *etc.*, the mobilities.

55. Importance of transference numbers.—According to the theory of complete dissociation we should expect that the conductance contributed in a 0.1 normal solution by the chloride ion would be nearly, if not quite, the same whether this ion was associated with hydrogen or with potassium ions, since the chloride ionic concentration is, according to this theory, the same in these two solutions. On the other hand, the Arrhenius theory requires a dissociation of 92.5 per cent. and 86.0 per cent. for the hydrochloric acid and potassium chloride solutions, respectively, and thus the contribution of the chloride ion to the conductance of the solution would be different, since the chloride-ion concentrations are not the same. As the conductance arising from the presence of the chloride ion in these solutions is equal to $n_{\text{Cl}^-} \Lambda$, where n_{Cl^-} is the transference number of the chloride ion, and Λ is the equivalent conductance, it is evident that accurate transference numbers are of importance in deciding between the two theories. MacInnes and Smith * have made accurate determinations of the transference numbers for three chlorides in solutions of concentration 0.1 normal at 25° C. Their results were as follows :—

Solution.	Equivalent Conductance (Λ).	Transference Number n_{Cl^-}	Λ_{Cl^-}
HCl	390.4	0.1680	65.59
KCl	129.0	0.5080	65.53
NaCl	106.8	0.6137	65.54

From these results it is inferred that the chloride ion contributes the same amount to the equivalent conductance in all these solutions, but although the figures prove that these chlorides have the same degree of dissociation, they do not prove that the dissociation is complete. MacInnes and Cowperthwaite † point out, however, that it is highly probable these substances are completely dissociated, since no properties, differing from those of the ions, have so far been assigned to the undissociated portion of strong electrolytes, although the theory of Arrhenius calls for the presence of considerable amounts of the electrolyte not in the ionic form. These experimenters have shown that if the chlorides are completely dissociated, then nitric acid and ammo-

* *Jour. Amer. Chem. Soc.*, 45, 2246 (1923) ; 47, 1009 (1925).

† *Trans. Farad. Soc.*, 23, 400 (1927).

nium nitrate must also be completely ionised. This conclusion is evident from the following tables :—

MOBILITY OF THE H^+ ION IN 0.1 NORMAL SOLUTIONS OF HCl AND HNO_3 AT $25^\circ C$.

Substance.	Equivalent Conductance Λ .	Transference Number n_{H^+} .	Λn_{H^+} .
HNO_3	385.0	0.8441	325.0
HCl	390.4	0.8320	324.8

MOBILITY OF THE NH_4^+ ION IN 0.10 NORMAL SOLUTIONS OF NH_4Cl AND NH_4NO_3 AT $25^\circ C$.

Substance.	Equivalent Conductance Λ .	Transference Number $n_{NH_4^+}$.	$\Lambda n_{NH_4^+}$.
NH_4NO_3	123.0	0.5130	63.1
NH_4Cl	128.6	0.4900	63.0

It will be observed that the product of the equivalent conductance and transference number is the same for the hydrogen ions, whether they are associated with nitrate or chloride ions. The same remark applies to the ammonium ions, and therefore the degrees of dissociation of the electrolytes are similar.

56. Absolute velocity of the ions.—If we consider the history of a single atom or ion, and average it over a long time, we may look upon α , the degree of ionisation, as measuring the fraction of all the time during which the atom is in an ionised condition, and it is obvious that this fraction must be the same as that obtained by averaging over all the molecules at a given instant. But an ion only travels under the influence of the electric field when it is free, for if it combines with an oppositely charged ion, it becomes neutral, and there is no electric force acting upon it, or rather, there are two equal and opposite forces. If, then, the ion when it is free, travels at the average speed u , it is only free for the fraction α of the whole time, and its velocity averaged over the whole time, whether free or not, is αu . In this way we obtain a conception that may be defined as the effective velocity. It may be regarded, either as the average velocity of a single ion over a long period of time, intervals of rest included, or as the average velocity of all the ions including those which are, for the time being, combined.

It is evident that the absolute ionic velocity can be determined

by means of two distinct methods termed, respectively, the direct and the indirect methods. The latter was evolved by Kohlrausch on his recognition that the ions migrated independently. Thus we have from equations (42) and (47),

$$u_K = \frac{n_K \Lambda_0}{F},$$

where u_K and n_K are now measured at infinite dilution, together with a similar expression for the velocity, u_A , of the anion at infinite dilution, so that the individual values of u_A and u_K can be calculated, if the equivalent conductance of the solution and the transference numbers, both at infinite dilution, are known; but as pointed out previously, the transference numbers vary with the concentration of the solution, and must be determined experimentally at some definite concentration. Although the theory of Hittorf's method of determining the transference number assumes that the difference produced in the concentrations around the electrodes is, in general, due entirely to the different ionic velocities, the action of complex ions must be taken into account, and therefore the true values of n_A and n_K for the various anions and kations are not known with any great degree of accuracy. Thus, the calculated values of the velocities may differ from those experimentally determined by means of the direct or moving boundary method, and this difference will be more marked in solutions such as magnesium sulphate, which contain complex ions, than in solutions of potassium chloride and other similar salts. Since the number of complex ions depends upon the solution concentration, the transference numbers cannot

TABLE XXXIII.

COMPARISON OF IONIC VELOCITIES BY THE DIRECT AND INDIRECT METHODS.

Ion.	Concentration of Solution in Gram Equivalents per Litre.	Velocity of Ion in Cm./Sec. per Volt/Cm. $\times 10^4$.	
		Observed.	Calculated from Kohlrausch's Data.
H ⁺ in chlorides	—	26.0	28.0
H ⁺ in acetates	0.07	.65	.48
$\frac{1}{2}$ Cu ⁺⁺ in chlorides	0.1	3.1	—
$\frac{1}{2}$ Ba ⁺⁺	0.1	3.9	3.7
$\frac{1}{2}$ Ca ⁺⁺	0.1	3.5	2.9
Ag ⁺	0.1	4.9	4.6
$\frac{1}{2}$ SO ₄ ⁻⁻	0.1	4.5	4.9
$\frac{1}{2}$ Cr ₂ O ₇ ⁻⁻	0.1	4.7	4.7

be estimated at infinite dilution unless the solution is so dilute that complex ions are absent.

In the absence of complex ions the velocities, as measured by the direct method, are equal to αu_A and αu_K , where α is the degree of ionisation, and u_A and u_K , the true ionic velocities at the concentration employed in the measurements. A comparison between the velocities of several ions, determined by the direct and indirect methods, is given in Table XXXIII.*

57. Dimensions of ions.—Assuming that at infinite dilution the motion of an ion through a solvent obeys Stokes's law, the radius, b , of an ion can be calculated from the equation,

$$b = \frac{\text{Force}}{6\pi\eta u}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (78)$$

where the force refers to that acting upon unit charge— 1.59×10^{-20} electromagnetic units—due to unit potential gradient, 1 volt per cm. = 10^8 absolute units, η is the coefficient of viscosity of the solvent, and u the velocity, in cms. per second, developed under this potential gradient. If, instead of u , we use the mobility, U , then,

$$b = \frac{8.15 \times 10^{-9}}{\eta U} \text{ cm.} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (79)$$

It is important to note that the radius calculated is that of the ion and its associated solvent molecules, *i.e.*, those molecules which behave as if rigidly attached to the ion, and which move with it. Hartley and Raikes † have determined the radii of ions, both in water and in methyl alcohol, from the mobilities at 25°C . by means of equation (79). Their results, together with the effective ionic radii in the crystal lattice, are given in Table XXXIV.

The ions of the alkali metals and of the halogens, which have the largest radii in the crystal lattice, also have the highest mobilities, while all the ions of the divalent metals possess, approximately, the same mobilities, in spite of a considerable increase in size with atomic number. This is usually explained by assuming that the ions are solvated, and that the degree of solvation of the small ions is greater on account of the more intense electric field around them, their mobilities being correspondingly reduced.

As pointed out by Hartley and Raikes, the radii of all ions in methyl alcohol are greater than in water, the increase in

* Whetham, *loc. cit.*

† *Trans. Farad Soc.*, 23, 393 (1927).

TABLE XXXIV.

IONIC RADIUS (ÅNGSTROM UNITS).

Ion.	In Water.	In Methyl Alcohol.	Crystal Lattice.	Ion.	In Water.	In Methyl Alcohol.	Crystal Lattice.
Li ⁺	2.30	3.78	0.72	$\frac{1}{2}$ Sr ⁺⁺	3.04	5.06	1.20
Na ⁺	1.79	3.27	1.01	$\frac{1}{2}$ Ba ⁺⁺	2.83	4.93	1.40
K ⁺	1.22	2.78	1.30	$\frac{1}{2}$ Zn ⁺⁺	3.36	5.02	0.60
Rb ⁺	1.17	2.60	1.50	$\frac{1}{2}$ Cd ⁺⁺	3.38	5.21	0.98
Cs ⁺	1.17	2.40	1.75	F ⁻	1.67	3.72	1.33
Ag ⁺	1.44	2.86	1.03	Cl ⁻	1.21	2.91	1.72
$\frac{1}{2}$ Mg ⁺⁺	3.44	5.19	0.75	Br ⁻	1.18	2.69	1.92
$\frac{1}{2}$ Ca ⁺⁺	3.05	4.98	1.02	I ⁻	1.20	2.45	2.19

apparent size being due, presumably, either to the larger solvent molecules, or to the greater number attached to the ion, the increase being more marked for the univalent than for the divalent ions. The influence of the ionic charge on the degree of solvation is shown by the fact that in both solvents all the divalent ions have the largest radii, although the radii in the crystal lattice vary. The silver ion, which is smaller than the rubidium and caesium ions in the lattice, has a lower mobility in both solvents, while the thallium ion, which is larger than the silver ion in the lattice, is also faster, having, approximately, the same mobility as rubidium and caesium ions.

Let b_A and b_K denote the radii of the anion and kation, respectively, at infinite dilution, and Λ_0 the equivalent conductance of the solution under the same conditions, then from equation (79),

$$\Lambda_0 = \frac{8.15 \times 10^{-9}}{\eta} \left(\frac{1}{b_A} + \frac{1}{b_K} \right). \quad (80)$$

If Λ_0 is known, the value of the harmonic mean of the ionic radii can be calculated, and compared with that determined by means of Debye and Huckel's formula.* Hartley and Bell† deduced these values for potassium, sodium and tetraethylammonium iodides in various solvents and the results which they obtained are given in Table XXXV. Although the numbers do not show any well-defined regularity, it is evident that the values of b , the harmonic mean of the radii, as calculated from Stokes's law, rarely differ from one another by more than a factor of two, whereas the values calculated with the help of Debye and Huckel's equation

* See section (146).

† *Trans. Farad. Soc.*, 23, 399 (1927).

show much larger variation. One interesting feature is the difference in behaviour of sodium and potassium iodides in pyridine.

TABLE XXXV.

RADII (HARMONIC MEAN) OF IONS IN SOLVENTS.

Solvent.	Potassium Iodide.		Sodium Iodide.		Tetraethylammonium Iodide.	
	$b \times 10^8$ (Debye).	$b \times 10^8$ (Stokes).	$b \times 10^8$ (Debye).	$b \times 10^8$ (Stokes).	$b \times 10^8$ (Debye).	$b \times 10^8$ (Stokes).
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.
Water	0.5	1.19	—	—	2.10	1.65
Methyl alcohol	1.19	2.55	—	—	1.69	2.48
Ethyl alcohol	3.26	2.92	3.69	3.07	3.88	2.87
Propyl alcohol	—	—	4.67	3.30	—	—
Ammonia	1.48	1.84	3.46	2.05	—	—
Acetone	4.65	2.84	4.22	2.86	6.55	2.47
Isoamyl alcohol	31.0	4.45	24.6	4.60	—	—
Sulphur dioxide	12.6	1.65	—	—	—	—
Pyridine	14.5	2.48	4.47	2.62	—	—

In general, we assume that an ion can be represented by an electrical charge, distributed with spherical symmetry within a sphere of radius b , and with respect to interionic collisions it may be regarded as a rigid sphere. If we denote by b_0 the nearest distance of approach of another ionic centre, then, as Scatchard * has pointed out, b and b_0 are not necessarily equal. Except for acids b_0 is always greater than b , and in most cases it is two or three times greater.

Martin † has calculated the ionic radius of various ions in benzonitrile, at 25° C., and compared his results with those obtained from Debye and Huckel's formula. The values agree, but are somewhat larger than those of the same ions in water and in methyl alcohol.

58. Complex ions.—The changes in concentration which take place in a solution near the electrodes when an electric current is passing, are, in some cases, very marked, and although the transference numbers of anions and kations should lie between zero and unity, we find that in some cases this is not so. Jahn, ‡ working with aqueous solutions of cadmium iodide, found that the transference number of the kation was practically constant for concentrations between 0.005 and 0.2 normal, while for higher

* *Trans. Farad. Soc.*, 23, 455 (1927).

† *Jour. Chem. Soc.*, 132, 3270 (1928).

‡ *Zeits. phys. Chem.*, 37, 673 (1901).

concentrations the value diminished, and at 0.5 normal it was negative; in other words, the cadmium ion apparently reverses the direction of its movement and now goes to the anode. It is necessary to assume that unaltered salt is attached to one of the ions, forming what is known as a complex ion, such as CdI_3^- . The movement of such complex ions carries more cadmium towards the anode than is simultaneously transported by the cadmium ions proper towards the kathode. McBain,* after taking into account all the data of conductance, freezing-point and transference measurements, concluded that in a 0.1 normal aqueous solution about 80 per cent. of the molecules were undissociated cadmium iodide molecules, and that approximately half of the number of anions were in the form CdI_3^- . Such solutions of cadmium iodide are poor conductors, the undissociated molecules uniting with the iodide ions to form the complex anions.

This is by no means an isolated example, most divalent ions taking part, to a certain extent, in such phenomena as those exhibited by the iodides. If a sufficient quantity of anion is added to a weak solution containing a divalent ion, the latter forms a complex anion, and we have the striking and significant result that the usual movement of the kation towards the kathode is apparently suppressed, or even reversed.

Onsager † has shown that bivalent binary electrolytes in water, particularly magnesium and cadmium sulphates, do not support his formula for the relationship between conductivity and concentration, and the same is true for solutions of nitrates in methyl alcohol. This lack of co-ordination is attributed to the presence of complex ions.

The sulphide ion reacts with excess of sulphur, forming a complex ion ‡ which is comparable with the complex iodide ion, and in concentrated aqueous solutions of the alkali selenides and tellurides the metallic ions form complex anions.§ Ions, similar in character to the complex sulphide and iodide ions, are also present in lead and antimony solutions.||

When a solution of potassium cuprocyanide is electrolysed, the concentration of the copper ions near the anode increases, the copper forming part of a complex negative ion. By means of transference measurements with ammoniacal copper sulphate solutions and silver chloride, Reychler ¶ has shown that the

* *Zeits. Elektroch.*, 11, 222 (1905).

† *Phys. Zeits.*, 28, 277 (1927).

‡ Küster, *Zeits. anorg. Chem.*, 43, 53 (1905); 44, 431 (1905).

§ Tibballs, *Jour. Amer. Chem. Soc.*, 31, 902 (1909), and Kraus, *ibid.*, 29, 1557 (1907).

|| Peck, *ibid.*, 40, 335 (1918).

¶ *Bull. soc. chim. belg.*, 28, 215, 227 (1914).

migration of each copper ion to the kathode is associated with the transport of four molecules of ammonia in the same direction and that the complex kation $\text{Ag}(\text{NH}_3)_2^+$ is transported as such.

McBain and Rysselberge* found that most of the divalent salts contained complex ions to some extent. For example, in a 0.05 normal solution of magnesium chloride, to which a sufficient concentration of chlorine ions had been added, the magnesium went to the anode just like cadmium, and probably for the same reason. These authors observed the migration of cadmium, magnesium, lithium, potassium and calcium ions in 0.05 normal solutions of one of their salts containing at least one type of divalent ion, adding in each case a sulphate or chloride solution of strength 0.95 normal. From the distribution of the electric current between the two salts, calculated from the known conductance data, an approximate value of the transference number was obtained, and it was found that the movement of the ions was such that in the majority of cases more of the metal was being carried to the anode than was migrating, as simple ion, to the kathode.

Whetham,† when measuring the ionic velocities by the direct method, found that with concentrated alcoholic cobalt solutions more than one boundary line appeared, and that the direction of motion of some of these lines was occasionally reversed. These results can only be explained by assuming the existence of complex ions, unaltered salt being attached to one or other of the simple ions.

Schreiner‡ has suggested that a complex is formed between a water molecule and a hydrogen ion, resulting in a complex ion H_3O^+ , known as oxonium. Various facts support this view. For example, an alcoholic solution of hydrochloric acid is a good conductor of electricity, but in acetone the acid gives a solution of low conductance. This difference in behaviour is difficult to explain, unless it is assumed that the oxonium ion is formed. Again, the addition of water to alcoholic solutions of the strong acids decreases the conductivity of the solution, but the addition of water to solutions of weak acids increases it, from which it may be inferred that oxonium is formed in the first case, the velocity of this ion being less than that of the normal hydrogen ion in alcohol.

Bruns§ and Thönnessen|| observed that the addition of iodine increased the conductance of aqueous solutions of cadmium

* *Jour. Amer. Chem. Soc.*, 50, 3009 (1928).

† *Phil. Trans.*, A, 184, 337 (1893); 136, 507 (1895).

‡ *Zeits. anorg. Chem.*, 121, 321 (1922); 135, 333 (1924).

§ *Zeits. f. Phys.*, 34, 751 (1925).

|| *Ibid.*, 41, 810 (1927).

iodide and of alcoholic solutions of cadmium, potassium and mercuric iodides. This increase seems to be brought about by the breaking down of the complexes present in the solutions. Sodium iodide does not form complex ions in acetone, or in mixtures of the alcohols with acetone, but lithium bromide does give rise to complexes when dissolved in acetone, although they are broken up on the addition of alcohol.

Nies * found that the addition of iodine increased the conductance of sodium iodide in mixtures of acetone and methyl alcohol, the effect diminishing as more alcohol was added. With solutions of potassium iodide and lithium chloride in pure alcohol, the addition of iodine increases the conductance only when the solutions are concentrated; in dilute solutions the effect, especially of much iodine, is in the opposite direction. The iodine breaks up complexes and simple molecules, and unites not only with the iodine of the iodides, but also with the other halogens, forming complexes like Cl—I_2 .

In connection with the formation of complex ions, it is interesting to examine whether the ions in solution approach as closely to each other as they do in gaseous molecules or in crystals, *i.e.*, is the distance separating oppositely charged ions so small that there is no molecule of the solvent between them? Hückel † calculated the value of the smallest distance to which the ions in solution can approach each other. The alkali chlorides showed the following sequence:—



which is exactly the reverse of that to be expected on the basis of the distances that the ions are separated in the crystal lattice. These oppositely directed sequences of the ionic radii in solution and in the crystal, respectively, can only be explained by supposing that, since the lithium ion certainly holds the water more strongly than the caesium ion, water molecules still intervene between the oppositely charged ions, even when the ions in solution approach each other as closely as possible. Fajans ‡ suggested, however, that direct contact of the ions, without intervening water molecules, exists, and he concluded that a certain proportion of the ions in the case of lithium chloride, for example, approach within a distance from each other which is distinctly less than the actual mean interionic distance— 5.52×10^{-8} cm. When the ions are separated by this mean distance, there is only room for one water

* *Zeits. phys. Chem.*, 138, 447 (1928).

† *Erg. exakt. Naturwiss.*, 3, 221 (1924).

‡ *Trans. Farad. Soc.*, 23, 365 (1927).

molecule between them, and these close approaches probably involve direct contact of the two ions. Whether these intimate approaches of the ions to each other involve the formation of neutral undissociated molecules, or of complex ions, is not known with any degree of certainty.

BIBLIOGRAPHY.

- Baborovsky, *Zeits. phys. Chem.*, **129**, 129 (1927).
Baborovsky and Wagner, *ibid.*, **131**, 129 (1928).
Bein, *ibid.*, **27**, 1 (1898).
Birkenstock, *ibid.*, **138**, 432 (1928).
Bjerrum, *Erg. exakt Naturwiss.*, **5**, 139 (1926).
Buchböck, *Zeits. phys. Chem.*, **55**, 563 (1906).
Creighton, *Jour. Amer. Chem. Soc.*, **45**, 1237 (1923).
Drucker and Krsnjau, *Zeits. phys. Chem.*, **62**, 731 (1908).
Falk, *Jour. Amer. Chem. Soc.*, **32**, 1555 (1910).
Frenkel and Finkelstein, *Zeits. f. Phys.*, **35**, 239 (1925).
Getman, *Jour. Amer. Chem. Soc.*, **30**, 721 (1908).
Gibbons and Getman, *ibid.*, **36**, 1630 (1914).
Gross and Halpern, *Phys. Zeits.*, **26**, 636 (1925).
Grüneisen, *Wiss. Abh. Phys. Tech., Reich., iv.*, 237 (1918).
Hevesey, *Zeits. Elektrochem.*, **27**, 21 (1921).
Hibben and Noyes, *Jour. Amer. Chem. Soc.*, **45**, 355 (1923).
Hopfgartner, *Zeits. phys. Chem.*, **25**, 115 (1898).
Lindemann, *ibid.*, **110**, 394 (1924).
Löb and Nernst, *Zeits. phys. Chem.*, **2**, 948 (1888).
MacInnes and Brighton, *Jour. Amer. Chem. Soc.*, **47**, 994 (1925).
Mather, *Amer. Chem. Jour.*, **26**, 473 (1901).
Mutzel, *Wied. Ann.*, **43**, 15 (1891).
Noyes, *Jour. Amer. Chem. Soc.*, **23**, 37 (1901).
Noyes and Kato, *ibid.*, **30**, 318 (1908).
Noyes and Sammet, *ibid.*, **24**, 944 (1902); **25**, 165 (1903).
Remy and Reisener, *Zeits. phys. Chem.*, **124**, 394 (1926).
Remy, *ibid.*, **118**, 161 (1925).
Smith, *Jour. Amer. Chem. Soc.*, **50**, 1904 (1928).
Sugden, *Jour. Chem. Soc.*, **130**, 174 (1926).
Schmick, *Phys. Zeits.*, **24**, 56 (1924).
Washburn and Millard, *Jour. Amer. Chem. Soc.*, **37**, 694 (1915).
Wessel, *Ann. d. Phys.*, **77**, 21 (1925).

CHAPTER V.

HOMOGENEOUS IONIC EQUILIBRIA.

59. Equilibria of mixed electrolytes.—We have already discussed the equilibrium conditions existing between the ions and undissociated molecules within an electrolytic solution, and we have seen that if $[M^+]$, $[X^-]$, $[MX]$ represent the concentrations of the kations, anions and undissociated molecules, respectively, in the solution of an electrolyte, represented by MX , then from equation (49),

$$\frac{[M^+] \cdot [X^-]}{[MX]} = K. \quad . \quad . \quad . \quad (81)$$

If, now, another electrolytic solution is added to the first one, there will be, as a rule, a change in the degree of ionisation in each electrolyte. This fact may be illustrated by considering what happens when two simple electrolytes, MX and MX_1 , containing one ion in common, are mixed together. The addition of MX_1 increases the concentration of the M^+ ions, and since the equilibrium constant K does not depend upon ionic concentration, other processes must occur which, in effect, decrease the numerator of the left-hand side of equation (81) and increase its denominator, until K is restored to its original value. In other words, undissociated molecules of MX must re-form and a similar change must occur in the other electrolyte. Thus, on mixing two electrolytic solutions containing a common ion, the degree of ionisation of each electrolyte is *lowered*.

Under certain conditions, however, no such change occurs, and the solutions may be mixed without thereby affecting the number or nature of the ions, or the mean conductivity. Any two solutions which fulfil these conditions are known as *isohydric solutions*,* and we may investigate the relationships that must exist between such solutions in the following manner:—

Let α_1 and α_2 , C_1 and C_2 , K_1 and K_2 be the degrees of ionisation, concentrations and equilibrium constants, respectively,

* See Arrhenius, *Wied. Ann.*, 30, 51 (1887); *Zeits. phys. Chem.*, 2, 284 (1888).

of the two isohydric solutions. Before mixing, we have from equation (49),

$$\frac{\alpha_1^2 C_1}{(1 - \alpha_1)} = K_1; \quad \frac{\alpha_2^2 C_2}{(1 - \alpha_2)} = K_2,$$

which may be written thus,

$$\frac{\alpha_1^2}{(1 - \alpha_1)v_1} = K_1; \quad \frac{\alpha_2^2}{(1 - \alpha_2)v_2} = K_2, \quad . \quad . \quad (82)$$

where $C_1 = \frac{1}{v_1}$ and $C_2 = \frac{1}{v_2}$. If the solutions contain a common

ion, and after mixing the degrees of ionisation remain unchanged, then the *total molecular volume** becomes $v_1 + v_2$, and the number of common ions therein is $\alpha_1 + \alpha_2$. Since the number of the ions, which are not common to the solutions, remains unchanged, we have from the mass action law,

$$\frac{(\alpha_1 + \alpha_2)\alpha_1}{(1 - \alpha_1)(v_1 + v_2)} = K_1, \quad . \quad . \quad (83)$$

and from equations (82) and (83),

$$\frac{(\alpha_1 + \alpha_2)v_1}{\alpha_1(v_1 + v_2)} = 1, \quad . \quad . \quad (84)$$

$$i.e., \quad \frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2} \quad \text{or} \quad \frac{\alpha_1}{C_2} = \frac{\alpha_2}{C_1}. \quad . \quad . \quad (85)$$

Since $\frac{\alpha_1}{v_1}$ and $\frac{\alpha_2}{v_2}$ are the respective concentrations of the common ion in the two isohydric solutions, it follows that, if these concentrations are equal, no change takes place in the degree of ionisation of either solution when they are mixed. Now weak electrolytes are very slightly ionised, and since in a mixture of weak electrolytes the ionisation fraction is still further reduced, we may put $1 - \alpha_1 = 1 - \alpha_2 = 1$, and therefore, from equation (82),

$$\frac{\alpha_1^2 v_2}{\alpha_2^2 v_1} = \frac{K_1}{K_2}.$$

Utilising equation (85) we have

$$\frac{v_1}{v_2} = \frac{C_2}{C_1} = \frac{K_1}{K_2}. \quad . \quad . \quad (86)$$

Thus two solutions of weak electrolytes are isohydric if the ratio of their concentrations before mixing is equal to the inverse ratio of their equilibrium constants.

* The molecular volume is that volume containing one mole of substance.

60. The conductivity of mixed electrolytes.—The conductance of solutions of weak acids depends chiefly upon the mobility of the hydrogen ions, from which it follows that the specific conductance of isohydric solutions containing the same hydrogen-ion concentration will be equal, and the same as that of a mixture of the solutions. In obtaining this result we assume that the anion conductance is so small that it can be neglected, but if it is necessary to take it into account, we may calculate the specific conductance of such a mixture in the following manner:—

Let σ_1, σ_2 , be the specific conductances of the two isohydric solutions before mixing, v' and v'' the volumes which are mixed. Then the first solution in the mixture has a specific conductance equal to σ_1' where

$$\sigma_1' = \frac{\sigma_1 v'}{v' + v''},$$

and similarly for the second solution,

$$\sigma_2' = \frac{\sigma_2 v''}{v' + v''},$$

so that the total specific conductance, being the sum of the individual specific conductances, is given by

$$\sigma_1' + \sigma_2' = \frac{\sigma_1 v' + \sigma_2 v''}{v' + v''}.$$

Thus if $v' = v''$, the specific conductance of the resulting mixture is the average of the specific conductances of the original solutions. Although this principle has been applied to mixtures of weak acids, it holds even for solutions which do not conform to Ostwald's law, such as strong electrolytes, and it appears that the isohydric principle can also be applied in these cases. In fact it has been used extensively to calculate the conductances of mixed strong electrolytes. Ruby and Kawai* found, however, that it did not apply to mixtures of aqueous solutions of hydrochloric acid, and potassium and sodium chlorides. They computed the apparent equivalent conductances of the mixtures at any given total concentration by means of the formula,

$$\Lambda = x\Lambda' + y\Lambda'' + (1 - x - y)\Lambda''',$$

where $\Lambda', \Lambda'', \Lambda'''$ are the equivalent conductances of the pure electrolytes in solutions of concentrations equal to the total electrolyte concentration of the mixture, and x, y and $(1 - x - y)$ are the

* *Jour. Amer. Chem. Soc.*, 48, 1119 (1926).

mole fractions of the electrolytes present. Their results, calculated from this formula, agree well with the experimental values at low concentrations.

The isohydric principle may be used to elucidate the interactions which occur between solutions of any two acids. Two solutions containing a common ion will so react on each other, when mixed, that they become isohydric, since this is the condition that the undissociated part of each component shall be in equilibrium with the ion common to both. To secure this condition in a mixture of a strong acid, like hydrochloric acid, and a weak one, like acetic, a large amount of the feebly dissociated acetic acid and a small amount of the highly dissociated hydrochloric acid must co-exist. Thus, when dilute solutions of hydrochloric acid and sodium acetate are mixed, acetic acid is formed, and this process continues until the two acids are isohydric. We see, therefore, that a large amount of undissociated acetic acid must be formed, most of the acetate being decomposed and the strong acid replacing the weak one.

Although the calculation of the conductances of mixtures formed from non-isohydric solutions is complicated, various experimenters have put forward formulæ for these conductances which agree fairly well with the experimental results. As a rule the conductance is less than the average value of the components, and the calculated value in the case of solvents of low specific inductive capacity is less than that determined experimentally. This is due, probably, to an increase in the dissociating power of the solvent, brought about by the addition of the second electrolyte.

Bray and Hunt* calculated the specific conductances of mixtures of sodium chloride and hydrochloric acid aqueous solutions by assuming that the equivalent conductance of each substance in the mixture is the same as in a solution of the pure substance at the same concentration. To determine the ion concentration within the mixture, *i.e.*, the concentration of the common ion, definite values were assigned to the conductance of the sodium, hydrogen, and chloride ions, *viz.*, 51.2, 348.2, and 75.8, respectively. The specific conductance, σ , of the mixture is then given by

$$1000\sigma = 127.0 (C\alpha)_{\text{NaCl}} + 424.0 (C\alpha)_{\text{HCl}},$$

where $(C\alpha)_{\text{NaCl}}$ and $(C\alpha)_{\text{HCl}}$ represent the ionic concentrations of the sodium and hydrogen ions, respectively, in the mixture. The procedure may be illustrated, by means of the following

* *Jour. Amer. Chem. Soc.*, **33**, 781 (1911).

example, for a mixture of 0.1 normal solutions of these electrolytes :—

100% NaCl HCl		Ion Concentration 1000C _± Na ⁺ H ⁺ Cl ⁻			Equivalent Conductance in Mixture. NaCl HCl		Specific Conductance 1000σ ohm ⁻¹ . NaCl HCl Total.		
79.7	89.9	79.7	89.9	169.6	101.2	381.1	10.12	38.09	48.21

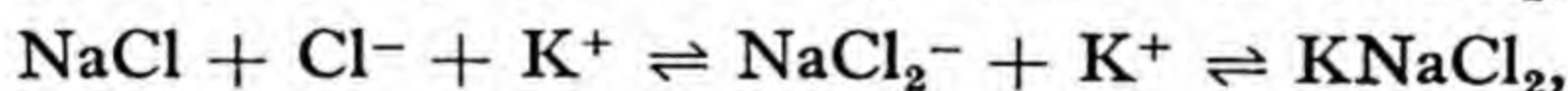
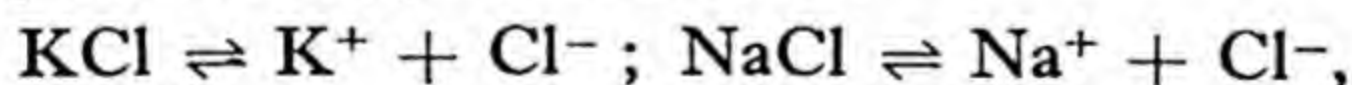
Their calculated and experimentally determined values of the specific conductances agreed remarkably well, as shown in Table XXXVI.

TABLE XXXVI.

SPECIFIC CONDUCTANCES OF ELECTROLYTIC MIXTURES.

Salt Concentration.			Measured Specific Conductance, 1000σ ohm ⁻¹ .	Calculated Specific Conductance, 1000σ ohm ⁻¹ .
NaCl.	HCl.	Total.		
·01998N	·04991N	·06989	21.75	21.89
·02000	·01999	·03999	10.157	10.27
·01998	·009988	·02997	6.253	6.307
·01998	·003996	·02398	3.889	3.919
·01998	·001997	·02198	3.101	3.118
·02000	·001000	·02100	2.709	2.721
·004995	·01250	·017495	5.651	5.678
·005000	·004996	·009996	2.632	2.650
·004996	·002697	·007693	1.621	1.630
·004997	·000999	·005996	1.011	1.016

In many cases complex ion formation accounts for the lack of agreement between the calculated and observed values of the conductances of mixtures. For example, when salts such as sodium and potassium chlorides are mixed in solution, the following equilibria may be attained :—



and the formation of the molecular or ion complexes decreases the conductance of the mixture. Therefore, the conductance of an equimolar solution of sodium and potassium chlorides, having a total concentration of one gram equivalent per litre, should be less than that calculated from the conductances of the pure salt solutions, each at the same concentration as the above. As Stearn * has pointed out, however, the effect of complex ion formation on the conductance of dilute solutions is very small.

* *Jour. Amer. Chem. Soc.*, 44, 670 (1922).

He worked with the halides of sodium and potassium at 25° C., and found that the differences between the calculated and observed values of the equivalent conductances were positive, and increased with the total salt concentration, but decreased generally for the iodides as compared with the chlorides. Some of his results are given in Table XXXVII.

TABLE XXXVII.

EQUIVALENT CONDUCTANCE OF MIXTURES OF SODIUM AND POTASSIUM HALIDES.

Concentration.	$\Lambda(\text{NaCl})$.	$\Lambda(\text{KCl})$.	$\Lambda(2\text{NaCl}, \text{KCl})$.		$\Lambda(\text{NaCl}, \text{KCl})$.		$\Lambda(\text{NaCl}, 2\text{KCl})$.	
			Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.
0.10N	106.82	128.34	113.99	114.12	117.58	117.46	121.16	120.97
0.50	93.92	117.06	101.63	101.51	105.50	105.16	109.35	109.10
1.0	86.36	111.60	94.77	94.14	98.98	98.75	103.19	102.82
2.0	75.90	105.70	85.83	85.17	90.80	90.12	95.77	95.20

Concentration.	$\Lambda(\text{NaBr})$.	$\Lambda(\text{KBr})$.	$\Lambda(2\text{NaBr}, \text{KBr})$.		$\Lambda(\text{NaBr}, \text{KBr})$.		$\Lambda(\text{NaBr}, 2\text{KBr})$.	
			Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.
0.10N	110.60	130.95	117.70	117.82	120.78	120.84	124.00	124.20
0.50	97.86	120.90	105.53	104.91	109.38	108.90	113.22	113.10
1.0	90.60	117.20	99.57	99.04	103.90	103.30	108.30	107.88
2.0	80.50	111.10	90.70	90.28	95.80	95.26	100.90	100.52
4.0	64.85	101.09	76.93	75.52	82.50	81.63	89.01	87.95

Concentration.	$\Lambda(\text{NaI})$.	$\Lambda(\text{KI})$.	$\Lambda(2\text{NaI}, \text{KI})$.		$\Lambda(\text{NaI}, \text{KI})$.		$\Lambda(\text{NaI}, 2\text{KI})$.	
			Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.
0.10N	109.40	130.56	116.50	116.60	120.00	120.15	123.50	123.50
0.50	98.83	122.20	106.62	106.20	110.50	110.12	114.40	114.11
1.0	92.53	118.58	101.21	100.68	105.55	104.90	109.89	109.55
2.0	83.66	113.69	93.67	93.02	98.67	98.10	103.68	103.15
4.0	68.36	103.74	80.15	79.36	86.05	85.20	91.95	90.70

61. Dissociation of water.—The specific conductance of very pure water is extremely small, about $0.7 \times 10^{-6} \text{ ohm}^{-1}$, and therefore it is ionised only to a slight extent. Arrhenius* regarded it as a weak acid, or base, containing hydrogen and

* *Zeits. phys. Chem.*, 1, 631 (1887).

hydroxyl ions in perfectly pure water, so that on dissolving in it alkali salts of weak acids, such as hydrocyanic acid, the resulting solutions have alkaline reactions, indicating that the ion CN^- is replaced by the hydroxyl ion and the compound potassium hydroxide is formed.

Now we may express the dissociation of water by means of the ordinary mass law, so that

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]},$$

where $[\text{H}^+]$, $[\text{OH}^-]$, and $[\text{H}_2\text{O}]$ represent the concentrations of hydrogen ions, hydroxyl ions, and undissociated water molecules, respectively. We may, however, regard $[\text{H}_2\text{O}]$ as constant, in which case

$$K_w = [\text{H}^+][\text{OH}^-],$$

K_w being called the ionic product of water. Its value, at $25^\circ \text{C}.$, is 10^{-14} , approximately. There are several methods whereby the value of K_w may be calculated, some of which will now be considered.

The specific conductance, σ_w , of water is given by the equation,

$$\sigma_w = \alpha N(U_{\text{H}^+} + V_{\text{OH}^-}),$$

where U_{H^+} and V_{OH^-} , the ionic conductances, or mobilities, are known. Hence, measuring σ_w experimentally, the value of αN , the number of gram ions of hydrogen per c.c. of water, may be calculated.

Another method, whereby the ionic product of water may be determined, is by examining its influence upon chemical reaction velocities. Thus, in aqueous solutions, methyl acetate is slowly decomposed into methyl alcohol and acetic acid, the hydroxyl ion of water being the active agent. The rate of this reaction is proportional to the number of hydroxyl ions present in the solution. Wijs * prepared an aqueous solution of methyl acetate, and titrated it at intervals with a standard alkali, in which the hydroxyl ion concentration was known. Since the free acetic acid, as it is formed, retards the action, it is necessary to estimate the transformation rate at the beginning of the process by some method of extrapolation.

Shields † studied the decomposition of an acetate solution into acetic acid and a base, which is brought about by the union of the ions of water, H^+ and OH^- , with the ions of the salt, the

* *Zeits. phys. Chem.*, 11, 492 (1893).

† *Ibid.*, 12, 167 (1893).

so-called *hydrolysis effect*. In this manner he determined the strength of water, acting as an acid, as compared with that of acetic acid. Since the degree of dissociation of the latter is known, that of water may be calculated. This method has also been employed by Noyes and his co-workers.*

The various methods used in determining the ionic product of water give concordant results, some of which, expressed in moles per litre, are shown in Table XXXVIII.

TABLE XXXVIII.
DISSOCIATION OF WATER.†

Temperature C.	Value of [H ⁺][OH ⁻] × 10 ¹⁴ .	Author.	Temperature C.	Value of [H ⁺][OH ⁻] × 10 ¹⁴ .	Author.
0°	·13	K.H.	30°	1·74	L.B.
0°	·089	Ka.	34°	2·1	K.H.
0°	·12	H.	40°	2·94	L.
0°	·14	L.B.	42°	3·65	K.H.
10°	·32	K.H.	50°	5·95	K.H.
10°	·28	H.	50°	5·66	H.
15°	·46	L.	50°	8·76	L.B.
18°	·64	N.	60°	12·60	L.B.
18°	·46	Ka.	70°	21·25	L.B.
18°	·59	H.	80°	35·04	L.B.
18°	·72	L.B.	90°	53·28	L.B.
25°	1·2	A.	100°	48	N.K.
25°	1·4	W.	156°	223	N.K.
25°	1·16	L.	218°	461	N.S.
25°	·82	Ka.	306°	168	N.S.

62. Solubility of electrolytes.—In a saturated electrolytic solution containing undissolved solute, equilibrium exists between the number of molecules passing to and from the solid into the solution. The undissociated salt in the solution plays the part of an intermediary between the ions and the solid, being in equilibrium with the ions on the one hand, and with the solid on the other. Consequently, as long as the solvent remains the same, the concentration of the undissociated salt is constant, however much the ionic concentrations may be separately varied by the introduction of other electrolytes, and the product of these

* *Jour. Amer. Chem. Soc.*, 29, 1402 (1907); 32, 159 (1910).

† K.H., Kohlrausch and Heydweiller, *Wied. Ann.*, 53, 234 (1894); Ka., Kanolt, *Jour. Amer. Chem. Soc.*, 29, 1414 (1907); H., Heydweiller, *Ann. d. Phys.*, 28, 511 (1909); L.B., Lorenz and Bohi, *Zeits. phys. Chem.*, 66, 748 (1909); L., Lowenherz, *ibid.*, 20, 293 (1896); N., Nernst, *ibid.*, 14, 155 (1894); A., Arrhenius, *ibid.*, 11, 823 (1893); W., Wijs, *ibid.*, 14, 189 (1894); N.K., Noyes and Kato, *ibid.*, 73, 20 (1910); N.S., Noyes and Sosman, *ibid.*, 73, 20 (1910).

ionic concentrations is also a constant. Considering a saturated solution of silver chloride, which is sparingly soluble in water, and applying the mass action law to the solution, we have

$$\frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]} = \text{constant}. \quad (87)$$

Since the concentration of the silver chloride molecules within the solution is constant, we may write

$$[\text{Ag}^+][\text{Cl}^-] = s_0, \text{ a constant}. \quad (88)$$

Van't Hoff * first suggested that this ionic product of a sparingly soluble electrolyte is constant, and it is known as the *solubility product*.

Now consider the theoretical solubilities † of two substances, containing a common ion, in the presence of each other in aqueous solution; for example, suppose that we add to the silver chloride solution another chloride salt. The concentration of the chloride ions is increased, and since the undissociated silver chloride concentration is constant, we see from equation (87) that the concentration of the silver ions must decrease. This can only be brought about by recombination of some silver and chloride ions to form undissociated silver chloride molecules. But the solution is already saturated, so that these silver chloride molecules, thus formed, must be precipitated. Hence the solubility of the silver chloride is, in general, decreased by the addition of a neutral salt containing an ion common to the salt already in solution, but the effect of the added solute depends upon its nature, as well as upon the nature of the solute already in solution. Thus the solubility of silver cyanide is increased by the addition of potassium cyanide, but this effect is due to the formation of a double salt, $\text{KAg}(\text{CN}_2)$.

With a sparingly soluble salt in solution, most of the dissolved molecules will be ionised, and the actual number of undissociated molecules will be extremely small, even in comparison with the total number of ions, which is also small. From this fact we see that the solubility is really determined by the number of kations, or anions, since they will be present in equivalent concentrations. When the second electrolyte is added, the solubility of the first one, namely silver chloride in our example, is determined by the silver ion concentration in the solution. In the first case it is evident from equation (88) that the solubility is proportional to

* *Zeits. phys. Chem.*, 3, 484 (1889).

† By solubility we mean the number of moles of solute dissolved per unit volume of solvent.

$\sqrt{s_0}$, since $[Ag^+] = [Cl^-]$, whereas after the addition of the second electrolyte, the solubility is proportional to $\frac{s_0}{[Cl^-]'}$, $[Cl^-]'$ being no longer equal to $[Ag]'$, where $[Cl^-]'$ and $[Ag^+]'$ are the new ionic concentrations, after the second electrolyte has been added.

This mutual influence of solubility was developed by Nernst * in the following manner :—

Let s denote the solubility of the first electrolyte in pure water, α being the degree of ionisation corresponding to this concentration. Then $s(1 - \alpha)$ and αs are the amounts of the electrolyte, undissociated and dissociated, respectively. If x is the concentration of the common ions in the second electrolyte, α' the degree of ionisation, and s' the solubility of the first electrolyte in the presence of this second one, then, since we assume that the concentrations of the undissociated molecules remain constant,

$$s(1 - \alpha) = s'(1 - \alpha'),$$

and, assuming that the mass action law holds, we have

$$\frac{(s\alpha)^2}{s(1 - \alpha)} = K,$$

and

$$\frac{s'\alpha'(s'\alpha' + x)}{s'(1 - \alpha')} = K.$$

Thus we get the relation,

$$(s\alpha)^2 = s'\alpha'(s'\alpha' + x),$$

from which
$$s' = -\frac{x}{2\alpha'} + \sqrt{s^2\left(\frac{\alpha}{\alpha'}\right)^2 + \frac{x^2}{4\alpha'^2}}. \quad (89)$$

Hence the solubility of the first electrolyte in the presence of the second one may be calculated from its solubility in the pure solvent and the amount of salt added. Noyes,† working with silver bromate solutions in the presence of silver nitrate or potassium bromate, verified this solubility formula. His results showed that equivalent mixtures of silver nitrate or potassium bromate change the solubility of silver bromate equally, and by amounts which agree with those calculated by means of equation (89), thus :—

* *Zeits. phys. Chem.*, 4, 372 (1889).

† *Ibid.*, 6, 241 (1890).

Amount of AgNO_3 or of KBrO_3 added.*	Solubility of AgBrO_3 on addition of AgNO_3 .	Solubility of AgBrO_3 on addition of KBrO_3	Calculated Solubility of AgBrO_3 .
0	·00810	·00810	·00810
·00850	·00510	·00519	·00504
·0346	·00216	·00227	·00206

In the case of tertiary electrolytes we have, from the mass action law

$$(s\alpha)^3 = s'\alpha'(s'\alpha' + x)^2,$$

where the notation is similar to that used for binary electrolytes. Noyes added the chlorides of magnesium, cadmium, zinc and copper, respectively, to lead chloride solutions, and assumed that lead chloride was dissociated to the same extent as that of the added chlorides, x being taken equal to the amount of chloride added multiplied by α' . The calculated and experimentally determined values of the solubility agree fairly well, as shown below :—

Amount of Salt added.	Value of α' .	Solubility s' .	
		Determined.	Calculated.
·05	·697	·0502	·0522
·10	·661	·0351	·0351
·20	·605	·0218	·0176

In deducing these various relations we have assumed that Ostwald's dilution law holds, but this law only applies to weak electrolytes. For strong electrolytes the equilibrium "constant," K , is by no means constant, increasing as the concentration is raised, so that the ratio of the ionised to the total substance dissolved becomes greater than the theoretical value. We can, however, proceed to find values of K for a substance at various concentrations and use the value at saturation to determine the solubility.

The assumption that the concentration of the undissociated molecules of an electrolyte remains constant with, or without, the presence of a second electrolyte has been attacked both theoreti-

* The amount of salt added is expressed in equivalents per litre of solution.

cally and experimentally by Arrhenius.* He showed that this assumption has no sound theoretical basis, and on determining the solubilities of silver salts of certain organic acids in water, and in aqueous solutions containing excess of the corresponding sodium salts, he found that the concentration of the undissociated molecules was not constant, but decreased with increased concentration.

In the case of a salt, such as silver chloride, which is very

TABLE XXXIX.†

SOLUBILITY OF SALTS IN THE PRESENCE OF OTHER SALTS.

Salt.	Added Salt.		Solubility.	Salt.	Added Salt.		Solubility.
	Nature.	Concentration.			Nature.	Concentration.	
ThCl	KCl NaCl NH ₄ Cl "	0	16.12	CaSO ₄	CuSO ₄	0	30.0
"		25	8.72	"	"	14.3	30.4
"		50	5.92	"	"	75.8	28.6
"		100	3.97	"	"	185.6	25.9
ThCl	HCl	25	8.69	Ba(BrO ₃) ₂	KBrO ₃	0	40.18
"	"	50	5.85	"	"	25.0	26.53
"	"	100	3.84	"	"	50.0	17.37
"	"	200	2.54	"	"	99.8	8.76
ThCl	KNO ₃	0	16.07	Ba(BrO ₃) ₂	KNO ₃	0	40.18
"	"	50	18.26	"	"	50	47.03
"	"	300	23.13	"	"	99.8	52.13
ThCl	K ₂ SO ₄	20	17.79	Ag ₂ SO ₄	AgNO ₃	25.0	39.09
"	"	100	21.37	"	"	49.8	28.45
"	"	300	26.00	"	"	99.6	16.96
CaSO ₄	NaCl	0	30.0	Ag ₂ SO ₄	KNO ₃	24.9	57.70
"	"	85.2	44.6	"	"	49.7	61.13
"	"	179.0	52.4	"	"	99.8	67.93
CaSO ₄	KNO ₃	0	30.64	Ag ₂ SO ₄	K ₂ SO ₄	25.0	50.66
"	"	52.67	40.17	"	"	50.0	49.35
"	"	123.6	48.20	"	"	100.0	48.04
CaSO ₄	MgSO ₄	0	30.64	Ag ₂ SO ₄	MgSO ₄	20.0	52.21
"	"	54.92	24.11	"	"	100.0	49.95
"	"	204.95	21.96	"	"	199.9	49.60
PbCl ₂	KCl	0	77.7	Ba(IO ₃) ₂	KNO ₃	0	1.579
"	"	100.0	34.1	"	"	10	1.826
"	"	200.0	21.9	"	"	200	3.190

* *Zeits. phys. Chem.*, 31, 197 (1899).

† See Noyes, *Jour. Amer. Chem. Soc.*, 46, 1098 (1924).

sparingly soluble in water, its solubility may be determined in the following manner. The concentration of the silver and chloride ions is very small, and on adding a potassium chloride solution of known strength, the total concentration of the chloride ions is practically equal to that in the potassium chloride solution, and is therefore known. The concentration of the silver ions in the mixed solutions may be determined from electromotive force measurements * and thus we have

$$[\text{Ag}^+] = \frac{s_0}{[\text{Cl}^-]},$$

from which s_0 , the solubility product, may be calculated. The solubility of the silver chloride may then be determined with the aid of equation (88).

The solubility of a strong electrolyte is generally depressed by adding another strong electrolyte containing an ion common to the first one, but if there is no such common ion, the solubility is increased. These facts are illustrated by the results shown in Table XXXIX. for the solubilities of various electrolytes. The concentration of the added salt, and the solubilities of the salt present as solid phase, are expressed in milli-equivalents per 1000 c.c. of solution.

63. Solubility in non-aqueous solvents.—In a general way the solubility relationships of electrolytes in non-aqueous solvents resemble those in water, *i.e.*, the solubility of a salt is diminished on the addition of a second salt with a common ion, while it is increased if the added salt has no common ion, but the magnitudes of these effects are much smaller in some solvents than in water. For instance, Kraus and Seward † measured the solubility of sodium chloride and of sodium bromide both in isopropyl alcohol and in acetone at 25° C. They obtained the following results, the concentrations being expressed in millimoles per litre :—

SOLVENT : ISOPROPYL ALCOHOL.

Solubility of NaCl . . .	·4246	·4159	·4050	·3817	·8539	1·5574
Concentration of NaNO ₃ . .	·0000	·0800	·1672	·4013	·3480	·3244
Solubility of NaCl . . .	·455	·481	·503	·547	·617	·734
Concentration of NH ₄ NO ₃ . .	·0000	·0985	·1839	·3537	·6938	1·4024

SOLVENT : ACETONE.

Solubility of NaBr . . .	·7677	·7597	·7462	·7629
Concentration of NaNO ₃ . .	·0000	·1371	·2286	·6602

* See Chapter VI.

† *Trans. Farad. Soc.*, **23**, 488 (1927).

King and Partington * used ethyl alcohol as the solvent and investigated the influence both of lithium iodide and of sodium thiocyanate on the solubility of sodium iodide at 25° C. The effects were similar to those usually found with aqueous solutions. They also calculated the dissociation of each of the two components, and the solubility data, so that the concentrations of the ionised and unionised molecules in the mixture could be determined. Their results, the solubility being expressed in grams of salt per 100 grams of solvent, are shown in Table XL. :—

TABLE XL.

SOLUBILITY OF NaI IN C_2H_5COOH IN THE PRESENCE OF NaCNS.

Solution.	Total Solu- bility.	Solu- bility of NaI.	Solu- bility of NaCNS.	Concen- tration of Na ⁺ 10 ⁴ .	Concen- tration of CNS ⁻ 10 ⁴ .	Concen- tration of I ⁻ 10 ⁴ .	Concen- tration of NaCNS × 10 ⁴ .	Concen- tration of NaI × 10 ⁴ .	Solu- bility Product [Na ⁺] [I ⁻] × 10 ⁷ .
NaI	42.85	—	—	3.869	—	3.869	—	17.07	1.497
1	42.98	41.81	1.17	3.901	.169	3.732	.883	16.60	1.456
2	43.11	39.18	3.93	3.988	.559	3.429	2.950	15.48	1.367
3	43.18	36.70	6.48	4.065	.896	3.169	4.858	14.45	1.288
4	43.16	36.25	6.91	4.078	.954	3.124	5.182	14.29	1.274
5	43.26	35.65	7.61	4.093	1.047	3.046	5.701	13.96	1.247
NaCNS	20.99	—	—	—	—	—	—	—	—

It will be observed that both the concentration of the undissociated sodium iodide and the solubility product decrease markedly on adding increasing amounts of sodium thiocyanate, although the concentration of the added salt is not large compared with the normal solubility of the iodide. These results are also interesting from another point of view. The total solubility of a salt in the presence of a second salt should never be less than the concentration of the undissociated part, but from Table XL. we see that the solubility of sodium iodide is depressed below the concentration value of the undissociated sodium iodide for a saturated solution of the pure salt. This confirms the theory of Arrhenius † that the undissociated salt concentration does not remain constant in the presence of another electrolyte.

Kendall ‡ investigated the solubility of salicylic acid in acetic, hydrochloric and formic acids. In the first case there was a continuous, regular increase of solubility as the concentration of the acetic acid increased; with hydrochloric acid solutions, of

* *Trans. Farad. Soc.*, 23, 522 (1927).

† *Proc. Roy. Soc., A*, 85, 200 (1911).

‡ *Loc. cit.*

increasing strengths, a sharp initial decrease was followed by a much smaller and more regular decrease, while with formic acid solutions a small initial decrease was, with increasing concentration, soon converted into a regular increase.

64. Osmotic phenomena.—The pressure which a gas exerts, at a given temperature, when a certain number of molecules are distributed throughout a given volume, is numerically identical with the osmotic pressure which would be exerted under the same conditions by the majority of substances dissolved in any liquid. In electrolytic solutions a fraction of the molecules is dissociated into ions which possess the property of independent movement and migration, and assuming that the osmotic pressure exerted by a dissolved solute arises from the impacts which the smallest individual components of the solute exert by their kinetic movements, it follows that the osmotic pressure is due both to the undissociated solute molecules and the ions actually present in the solution. In the case of a binary electrolyte, for example, the osmotic pressure of the solute, if it is completely dissociated, is double that which would be exerted if the molecules were not ionised, the other conditions remaining the same in the two cases. Those molecules, whose ions are free to move independently of one another, were designated by van't Hoff as *active*, and the undissociated molecules, *inactive*. He assumed that at very great dilution all of the inactive molecules of an electrolyte are converted into the active form. Van't Hoff denoted the ratio of the osmotic pressure actually exerted by a solute, to the osmotic pressure it would exert if it consisted entirely of non-dissociated molecules, by i . Thus, if there are C_0 inactive molecules and C active ones present, and one molecule can dissociate into n ions, then,,

$$i = \frac{C_0 + nC}{C_0 + C}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (90)$$

and it is evident that i represents the ratio of the actual osmotic pressure to the normal value if no dissociation occurs. In addition, if α is the fraction of the molecules ionised, then,

$$\alpha = \frac{C}{C_0 + C} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (91)$$

65. Freezing-point temperature depression.—It has been shown in section (12) that the depression of the freezing-point temperature of a solution is proportional to the osmotic pressure exerted by the solute, and it is evident, therefore, that

the van't Hoff factor, i , may be calculated by measuring the lowering, δT , of the freezing-point temperature of an aqueous solution, containing one mole of a given substance in 1,000 grams of water, and dividing the result by 1.858, the molecular depression for non-dissociated substances. Since one mole of solute per 1,000 grams of solvent is, in many cases, unrealisable in practice, the lowering of the freezing-point temperature is carried out with much more dilute solutions. This observed lowering is then altered in a simple proportion to the value it would have if one mole of solute were dissolved in 1,000 grams of solvent, the conditions remaining the same in both cases.

It is a matter of some difficulty to measure the freezing-point temperature of very dilute solutions with sufficient percentage accuracy. For example, a 0.01 normal aqueous solution of potassium chloride freezes at -0.0361°C. , so that an error of only 0.001°C. in the equilibrium temperature corresponds to an error of 3 per cent. in the observed lowering, and, accordingly, to an uncertainty of 6 per cent. in the degree of ionisation derived therefrom. The essentials of accurate freezing-point determinations are: (a) rapid and certain attainment of a practically stationary temperature equilibrium; (b) accurate and convenient measurement of the temperature; (c) determination with sufficient exactness of the concentration of the equilibrium solution. These conditions* are realised by (a) thoroughly mixing the solution with a large amount of broken ice; (b) measuring directly, with a sensitive thermo-element and potentiometer outfit, the difference between the equilibrium temperatures of the ice-solution and of the ice-water; (c) analysing the equilibrium solution by means of interferometers.

Having determined the value of i from the measured value of δT , corresponding to a certain concentration of the electrolyte in water, it is evident that α , the dissociation at this concentration, may be calculated, since, from equations (90) and (91) we have

$$i = 1 + (n - 1)\alpha. \quad . \quad . \quad . \quad (92)$$

The hypothesis of complete dissociation infers that the osmotic pressure effects for binary electrolytes should have double their normal value, and since the normal value of the molecular depression of the freezing-point temperature is 1.858 we should expect twice this value, *viz.*, 3.716 for all such completely ionised electrolytes, a number to which all the observed molecular depressions closely approximate. Similarly, the tertiary electrolytes

* See Adams, *Jour. Amer. Chem. Soc.*, 37, 481 (1915).

should yield a theoretical molecular depression 5.574, and although the experimental numbers differ from this value, the error is in the right direction, since even in the most dilute solutions employed, the ionisation is still far from complete with the salts containing divalent ions. It is a striking fact that, as the concentration decreases, the molecular depression of the freezing-point temperature increases, and approaches a limiting value, which, in the case of salts of different types, corresponds with the ionic structure of these salts, and is in agreement with the fundamental ionic reactions assumed in the ionic theory. In some cases the theoretical values are exceeded, but these discrepancies are very small.

Values of the molecular depressions for various electrolytes in aqueous solutions, at different concentrations, are given in Table XLI. :—

TABLE XLI.

MOLECULAR DEPRESSION OF THE FREEZING-POINT TEMPERATURE.

Concentration.	.005N.	.010N.	.020N.	.050N.	.100N.	.200N.	.500N.
NH ₄ Cl	3.617	3.582	3.544	3.489	3.442	3.392	—
KCl	3.648	3.610	3.564	3.502	3.451	3.394	3.314
NaCl	3.629	3.600	3.568	3.516	3.478	3.424	3.358
HCl	3.700	3.669	3.637	3.591	3.555	—	—
BaCl ₂	5.196	5.120	5.034	4.900	4.784	4.660	—
CdCl ₂	—	4.796	4.710	4.420	4.104	3.852	—
CaCl ₂	—	—	5.112	4.966	4.886	4.832	—
ZnCl ₂	5.412	5.286	5.148	4.954	4.792	4.620	—
KBr	—	—	3.584	3.509	3.455	3.404	3.337
NaBr	—	—	3.611	3.551	3.507	3.463	—
CdI ₂	—	4.062	3.864	3.344	2.694	2.266	—
KNO ₃	—	3.532	3.493	3.411	3.303	3.168	—
NaNO ₃	—	3.536	3.502	3.446	3.393	3.329	—
Pb(NO ₃) ₂	5.164	5.016	4.844	4.548	4.270	3.960	3.428
Cd(NO ₃) ₂	5.380	5.278	5.204	5.154	5.140	—	—
KClO ₃	—	3.556	3.513	3.435	3.334	—	—
NaBrO ₃	—	—	3.545	3.492	3.419	—	—
KIO ₃	3.606	3.555	3.497	3.397	3.274	—	—
K ₂ SO ₄	5.308	5.198	5.040	4.776	4.568	4.324	3.948
Na ₂ SO ₄	—	—	5.078	4.810	4.592	4.344	3.944
H ₂ SO ₄	5.052	4.814	4.584	4.300	4.112	3.940	3.736
CdSO ₄	3.080	2.916	2.744	2.496	—	—	—
CuSO ₄	3.003	2.871	2.703	2.448	—	—	—
MgSO ₄	3.148	3.006	2.854	2.638	2.460	2.270	2.008
ZnSO ₄	3.094	2.940	2.766	—	—	—	—
KOH	3.706	3.684	3.654	3.578	3.458	—	—

66. Boiling-point temperature elevation.—From the standpoint of thermodynamics, the principle of the boiling-point temperature elevation ranks equally with that of the freezing-point method as a means of measuring the ionisation of dissolved substances. It has the one decided advantage that it can be applied to solutes in all solvents. Except as a means of determining molecular weights of dissolved substances, the use of this method has been neglected for many reasons. Amongst these are (a) the unavoidable superheating of the liquid and vapour; (b) uncontrollable fluctuations in the barometric pressure during a series of determinations; (c) the introduction of impurities from the air, and changes in concentration due to the presence of the solvent in the vapour phase. Cottrell * conceived the idea of actually pumping up the boiling liquid and allowing it to flow over a thermometer bulb suspended in the vapour phase. Washburn and Read † also employed this method, and they attempted to avoid superheating, and to ensure quiet boiling, by placing in each boiling flask a small quantity of fragments of porcelain. Pearce and Hicks ‡ used a delicate thermocouple to indicate the temperature, the electromotive forces produced being proportional to the difference between the boiling-point temperatures of the solution and pure solvent.

It has been shown in section (11) that for a concentration of one mole of undissociated solute per 100 grams of water, the boiling-point temperature elevation is 5.15°C. , so that if δT is the molecular elevation obtained with an electrolytic solution, the van't Hoff factor, i , is equal to $\frac{\delta T}{5.15}$, and hence α , the degree of dissociation, may be calculated by means of equation (92).

A large number of measurements have been made on electrolytes in non-aqueous solvents, using this boiling-point method, but only a few of these observations were made with solutions in which the dilution was carried far enough to justify the assumption of complete ionisation. Measurements with strong solutions are not of much use because, as soon as the solute particles approach closely to one another, the osmotic pressure is not given by the ideal gas laws.

Walden and Centnerszwer § measured the molecular elevation of the boiling-point temperature of various electrolytes in liquid

* *Jour. Amer. Chem. Soc.*, **41**, 721 (1919).

† *Loc. cit.*, **41**, 729 (1919).

‡ *Jour. Phys. Chem.*, **30**, 1678 (1926).

§ *Zeits. phys. Chem.*, **39**, 513 (1902).

sulphur dioxide, and the values which they obtained for van't Hoff's factor, i , are given in Table XLII. :—

TABLE XLII.

VALUES OF VAN'T HOFF'S FACTOR FOR ELECTROLYTES DISSOLVED IN LIQUID SO_2 .

Substance.	Values of i at Concentrations			
	1 N.	0.5 N.	0.25 N.	0.05125 N.
KI	0.42	0.55	0.63	0.86
NH_4I	0.41	0.53	0.64	0.82
RbI	0.52	0.61	0.73	0.85
NH_4CNS	0.29	0.40	—	—
KCNS	0.41	0.49	0.60	0.71

67. Thermal properties of electrolytes.—The solution of substances is accompanied by liberation or absorption of heat. The heat change produced when a mole of a solute is dissolved in enough solvent to form a given solution is called the *total heat of solution*. It is obvious that if the substance is dissolved to saturation, the change of heat is always more or less different from the heat of solution, as defined above. If we know the solubilities at two different temperatures, the heat absorbed or liberated when the solute is dissolved to saturation may be calculated as follows :—

Since every substance has a definite solubility in a definite solvent at a definite temperature, we may write

$$s = K, \quad . \quad . \quad . \quad . \quad (93)$$

where s is the solubility, or concentration, of the saturated solution, and K is the equilibrium constant at a temperature T . This equation assumes that no dissociation occurs, and since during solution the volume of the liquid is not appreciably altered, no external work is done, so that from equations (33) and (93) we have

$$H_v = RT^2 \frac{\partial}{\partial T} \log s. \quad . \quad . \quad . \quad . \quad (94)$$

Assuming further that H_v does not change with temperature, which is, in fact, only approximately true, we have on integrating equation (94),

$$\log s_1 - \log s_2 = \frac{H_v}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right],$$

where s_1 and s_2 are the solubilities of the substance at temperatures T_1 and T_2 , respectively. Thus van't Hoff * calculated the value of H_v to be 6,830 calories per mole for succinic acid in water, the solubilities being 2.88 and 4.22 at absolute temperatures, 273° and 281.5° , respectively. This value agrees well with that found experimentally by Berthelot,† namely, 6,700 calories per mole.

If the solute dissociates, such as happens with electrolytes, then equation (93) must be replaced by one which takes this phenomenon into account. Thus, for a binary electrolyte we

have $s^2 = K$,

and $H_v = 2RT^2 \frac{\partial}{\partial T} \log s$.

Knowing the relation between H_v and T , and also the manner in which the solubility changes with temperature, the value of H_v can be accurately determined. Values of the heat of solution, calculated by van't Hoff, agree very well with those determined experimentally by Thomsen,‡ as shown in Table XLIII.

TABLE XLIII.
HEATS OF SOLUTION.

Substance.	Temperature (Degrees absolute).		Solubility (Grams per Cent.).		Heat of Solution (Calories per Mole).	
	T_1 .	T_2 .	s_1 .	s_2 .	Observed.	Calculated.
Succinic acid .	273°	281.5°	2.9	4.22	6,700	6,500
Benzoic acid .	277.4°	348°	0.182	2.193	6,500	6,700
Salicylic acid .	285.5°	354°	0.16	2.44	8,500	8,900
Oxalic acid .	273°	283°	5.2	8.0	8,500	8,200
Boric acid .	273°	285°	1.95	2.92	5,600	5,200
Barium hydrate .	273°	283°	1.5	2.22	15,200	16,300
Aniline .	289°	308°	3.1	3.6	100	700
Amyl alcohol .	273°	291°	4.23	3.0	-2,800	-3,300
Phenol .	274°	318°	7.1	10.2	2,100	1,400
Potassium bichromate .	273°	283°	4.6	7.4	17,000	17,300
Potassium chlorate .	273°	288.4°	3.3	6.03	10,000	11,000
Barium nitrate .	273°	282°	5.2	7.0	9,400	8,800
Mercuric chloride	283°	323°	6.6	11.8	3,000	3,000

* *Lois de l'équilibre*, 37 (1885).

† *Thermochimie* (1897).

‡ *Thermochemische Untersuchungen*, I., 149 (1882).

In the equation

$$H_v = RT^2 \frac{\partial}{\partial T} (\log K)_v \quad . \quad . \quad . \quad (95)$$

H_v is the sum of the heat contents of the substances produced during any reaction, less the sum of the heat contents of the substances consumed, and therefore this equation affords a means of calculating the total heat change which occurs during the dissociation of an electrolyte in any solvent. It may also be written in the form,

$$\frac{\partial (R \log K)_v}{\partial \left(\frac{1}{T}\right)} = -H_v,$$

where H_v is the heat *absorbed*, and if the value of K is known at different temperatures, we may plot values of $R \log K$ against those of $\frac{1}{T}$. If H_v is constant, the resulting graph should be a straight line, but in most cases, a very pronounced curve is obtained, even for a small temperature range. The slope of the curve at any temperature gives, at once, H_v , the heat absorbed at that temperature in the dissociation of one mole of the electrolyte. Lewis and Randall,* considering constant pressure conditions, have shown that when the values of $R \log K$ for ammonium hydroxide are plotted against $\frac{1}{T}$, the resulting relationship is almost linear at the lower temperatures and that

$$H_v = 16,500 - 52.5T,$$

from which the heat of dissociation at 18° C. is calculated to be 1,200 calories. This agrees with Thomsen's experimentally determined value, 1,200-1,400 calories.†

68. The heat of dissociation of water.—It is evident that if the dissociation constant of water is known at different temperatures the quantity of heat, H_v , that must be absorbed, whenever one mole of water dissociates into its constituent ions, may be calculated as shown in the previous section. If we consider a small temperature range, and assume that the heat of dissociation throughout this range remains constant, then on integrating equation (95),

$$-\frac{H_v}{T} = R \log K + \text{constant} \quad . \quad . \quad . \quad (96)$$

* *Thermodynamics*, p. 313 (1923).

† *Loc. cit.*

Michaelis * has interpolated values of $\log K$ at different temperatures, and taking his values, *viz.*, $\log_{10} K$ at $24^\circ \text{C.} = -13.925$, $\log_{10} K$ at $26^\circ \text{C.} = -13.860$, and remembering that R is equal to 1.989 calories per mole per degree C., we have

$$H_v = 13,275 \text{ calories per mole}$$

as the average value of the heat of dissociation of water over the temperature range 24°C. to 26°C. Thus, we may assume this value to hold at 25°C. Wörmann † measured the heat of dissociation at this temperature and obtained the value 13,410 calories.

If we assume that the heat of dissociation is a linear function of the temperature, *viz.*,

$$H_v = H_v^0 + aRT,$$

where a is a constant, and H_v^0 is the value of H_v at $T = 0$, then, substituting for H_v in equation (95) and integrating,

$$\log \frac{K_1}{K_2} - a \log \frac{T_1}{T_2} = \frac{H_v^0}{R} \cdot \frac{T_1 - T_2}{T_1 T_2},$$

from which H_v^0 and a may be calculated if K_1 and K_2 are known at the temperatures T_1 and T_2 , respectively. In this way Noyes ‡ obtained the expression

$$H_v = 28,460 - 49.5 T \quad . \quad . \quad . \quad (97)$$

for the heat of dissociation of water at a temperature T . His results were as follows :—

Temperature.	Heat of Dissociation, H_v .	Temperature.	Heat of Dissociation, H_v .
0°C.	14,950 calories.	100°C.	9,995 calories.
18°	14,055 „	128°	8,610 „
25°	13,710 „	156°	7,225 „
50°	12,470 „	218°	4,155 „
75°	11,230 „	—	—

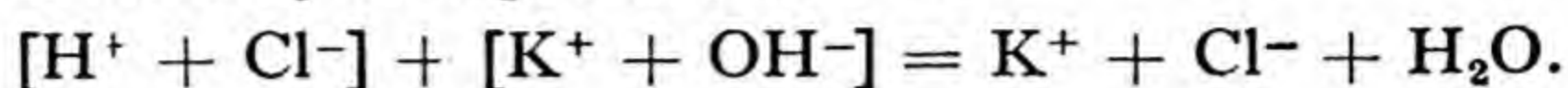
69. The heat of neutralisation.—Since changes in temperature affect the value of the equilibrium constant, it is only when salts are completely ionised that no change in temperature occurs when solutions are mixed. If one component, before or after mixing, is slightly dissociated, combination of the ions occurs,

* *Die Wasserstoffionenkonzentration*, Berlin (1922).

† *Ann. d. Phys.*, 18, 793 (1905).

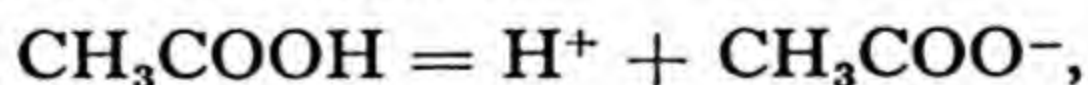
‡ Carnegie Publications, No. 63 (1907).

and heat will be liberated, or absorbed. Now the dissociation theory postulates that the neutralisation of an acid by a base may be represented by an equation, such as



Thus, since the ionic product of water is extremely small, and the concentrations of the hydrogen and hydroxyl ions are both very small, practically all of them unite to form undissociated water molecules. From this it follows that the heat changes occurring are brought about by this formation of water molecules, and therefore, when a gram-equivalent of a strong acid (completely ionised) is neutralised with a gram-equivalent of a strong base (also completely ionised), the heat liberated is that which is produced when one mole of water is formed, namely, 13,710 calories at 25° C.

This fact also explains Thomsen's results.* He found that when a strong acid reacted with an equivalent quantity of a strong base in dilute solution, the heat evolved was always about 13,700 calories, whatever the acid and base used, but in reactions with the weaker acids and bases the heat changes diverged from this normal value. As a rule, the salts formed from such acids and bases are more fully dissociated than the *reactants*, and thus ions will be formed during the process. For example, acetic acid is dissociated only to a slight extent, and heat must be absorbed to complete ionisation. If α is the fraction of the molecules ionised, heat equal to $(1 - \alpha)H_v$ must be supplied to complete the ionisation, where H_v is the heat of ionisation of acetic acid; and thus to obtain the heat of neutralisation of this acid $(1 - \alpha)H_v$ must be subtracted from the heat of water formation. The dissociation constant of acetic acid, calculated from Kendall's conductivity measurements,† is 0.0000184 at 25° C., and assuming that the value of K for the ions and molecules in solution is the same as that for the atoms and molecules in the gaseous form, *i.e.*, assuming the particles in solution behave as a perfect gas, we find that for the reaction



the energy absorbed, as given by equation (32), is 6,463 calories at 25° C. Strictly speaking, this is the energy absorbed under constant pressure conditions, but as the change in volume during the reaction is extremely small it may also be taken as the heat absorbed under constant volume conditions.

Thomsen used some sulphuric acid solutions, in his experi-

* *Loc. cit.*

† *Medd. Vetens. Nobelinst*, 2, 38 (1911).

ments on neutralisation, in which the fraction of the sulphuric acid molecules ionised was only about 0.5. With these he found that the heat of neutralisation was greater than the normal value. Thus heat must be evolved during dissociation of sulphuric acid into its constituent ions.

In the case of many acids the equilibrium constant, K , decreases with temperature so that the heat of dissociation is negative (heat is evolved) and the heat of neutralisation is greater than the normal value. With the aid of equation (96) Arrhenius* determined the value of K at different temperatures, and so measured the heats of dissociation of various electrolytes. Knowing the coefficient of ionisation he then calculated $(1 - \alpha)H_v$, the heat evolved, or absorbed, by the completion of the dissociation of the electrolyte, and added it to the heat of dissociation of water. The result should be equal to the heat of neutralisation of the electrolyte, and as Table XLIV. shows, there is good agreement between the observed and calculated values.

TABLE XLIV.

HEATS OF NEUTRALISATION AT 21.5° C. (CALCULATED AND OBSERVED).

Acid.	Heat of Neutralisation.		Acid.	Heat of Neutralisation.	
	Observed.	Calculated.		Observed.	Calculated.
	Calories.	Calories.		Calories.	Calories.
Hydrochloric acid . . .	-13,447	-13,740	Butyric acid . . .	-13,957	-13,800
Hydrogen bromide . . .	-13,525	-13,750	Succinic acid . . .	-12,430	-12,400
Nitric acid . . .	-13,550	-13,680	Dichloroacetic acid . . .	-14,930	-14,830
Acetic acid . . .	-13,263	-13,400	Phosphoric acid . . .	-14,959	-14,830
Propionic acid . . .	-13,598	-13,480	Hypophosphorus acid . . .	-15,409	-15,160
			Hydrofluoric acid . . .	-16,320	-16,270

Recently Richards, Mair and Hall† measured, at 20° C., the heats of neutralisation of acids by sodium hydroxide, and obtained the following results :—

Acid.	Heat of Neutralisation.	Acid.	Heat of Neutralisation.
	Calories.		Calories.
Acetic acid	-12,995	Hydrochloric acid . . .	-13,924
Citric acid	-12,753	Hydrogen bromide . . .	-13,856
Monosodium dihydrogen citrate . . .	-12,710	Hydrogen iodide . . .	-13,797
Disodium monohydrogen citrate . . .	-13,077	Nitric acid	-13,851

* *Zeits. phys. Chem.*, 4, 96 (1889) ; 9, 339 (1892).† *Jour. Amer. Chem. Soc.*, 51, 731, 737, 740 (1929).

the specific gravity of the solution, referred to water, could be calculated. Assuming that the specific refractions of the salt and of the water are additive, they computed both the specific and *molecular refractions*, Mk , of the salt in solution by means of the following equations:—

$$k = \frac{1}{p} \left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \cdot \frac{100}{\rho_s} - \frac{\mu_w^2 - 1}{\mu_w^2 + 2} \cdot \frac{100 - x}{\rho_w} \right),$$

$$Mk = \frac{M}{p} \left(\frac{\mu_s^2 - 1}{\mu_s^2 + 2} \cdot \frac{100}{\rho_s} - \frac{\mu_w^2 - 1}{\mu_w^2 + 2} \cdot \frac{100 - x}{\rho_w} \right),$$

where k = specific rotation of the salt in solution,
 M = molecular weight, x = percentage of salt,
 μ_s = refractive index of solution at 25°C. ,
 μ_w = refractive index of water at 25°C. ,
 ρ_s = density of solution at 25°C. ,
 ρ_w = density of water at 25°C.

As shown in Table XLV. the specific refractions are practically independent of the solution concentrations, as they should be if the additive principle is true:—

TABLE XLV.

SPECIFIC AND MOLECULAR REFRACTIONS OF SALTS.

Salt.	Per cent. of Salt in Solution.	Refractive Index of Solution. (μ_s).	Specific Refraction of Salt. (k).	Salt.	Per cent. of Salt in Solution.	Refractive Index of Solution. (μ_s).	Specific Refraction of Salt. (k).
LiCl	·6254	1·33388	·2093	LiBr	·3889	1·33307	·1412
	·9688	1·33460	·2088		6·1940	1·34200	·1408
	5·7352	1·34465	·2073		18·190	1·36254	·1415
	13·1099	1·36024	·2045	KBr	·9874	1·33370	·1277
NaCl	·5280	1·33342	·1605		8·8542	1·34327	·1254
	1·1068	1·33438	·1592		21·017	1·35984	·1251
	5·4131	1·34179	·1582	NaI	·7469	1·33362	·1299
	14·344	1·35747	·1582		6·8272	1·34278	·1300
KCl	·9466	1·33376	·1544		30·418	1·38783	·1292
	4·8340	1·33896	·1500	KI	·9151	1·33367	·1274
	13·755	1·35122	·1517		8·5864	1·34422	·1295
	21·770	1·36238	·1513		25·604	1·37194	·1289

Any deviation from the principle of additivity which is found in practice must be regarded as an indication of influences exerted by the components upon each other, such influences, for example, as may be exerted by the ions on the solvent

molecules in the case of electrolytic solutions. Fajans and Joos,* from the specific refraction of the perfect gases and of the alkali-halogens in solution, obtained individual values of the refraction for alkali and halogen ions, and hence also for many other ions in solution. The values thus obtained agree, to a first approximation, with those found by Wasastjerna † on the basis that, for the hydrogen ion in very dilute aqueous solution as an electron-free structure, the refraction has a null value.

Fajans and Joos showed that the specific refraction of anions is lowered by neighbouring cations, while the refraction of cations is increased by neighbouring anions. Similar effects are produced on the refraction of water in the immediate neighbourhood of the ions. For example, if the molecular refraction of aluminium chloride in very dilute aqueous solutions is calculated in the usual manner, that is by subtracting from the molecular refraction of the solution that of water, the value 24.6 is obtained. Now the three chloride ions have a molecular refraction equal to $3 \times 9.00 = 27.00$. Hence for the aluminium ion there results the impossible value, $24.6 - 27.0 = -2.4$. Since free gaseous aluminium ions must have a molecular refraction of about 0.17, the anomaly can only be explained on the supposition that the molecular refraction of the water has been greatly decreased by the strong electric field due to the small and highly charged aluminium ion. This decrease will be distributed among the several water molecules surrounding the aluminium ion in the dilute solution.

The specific refraction of a solution will vary as the ions approach more closely to one another, thereby displacing the water and uniting to form undissociated molecules, or complex ions. Association of the ions will also affect the refraction.

Fajans ‡ plotted the molecular refractions at various concentrations (Fig. 19), and extrapolated the results to infinite dilution. The values thus obtained, at zero concentration, proved to be strictly additive within the limits of experimental error. With increasing concentration there is in the case of halides a decided decrease in refraction. On the other hand, potassium fluoride shows an increase in refraction as the concentration increases. The values of the molecular refraction, k_m^0 , at infinite dilution, and of $\delta k_m = k_m^{5N} - k_m^0$, where k_m^{5N} is the molecular refraction of a 5 normal solution for various salts at 25° C., are given in

* *Zeits. f. Phys.*, **23**, 1 (1924).

† *Zeits. phys. Chem.*, **101**, 193 (1922).

‡ *Trans. Farad. Soc.*, **23**, 364 (1927).

Table XLVI. The refractive index was measured with respect to the sodium D line radiation.

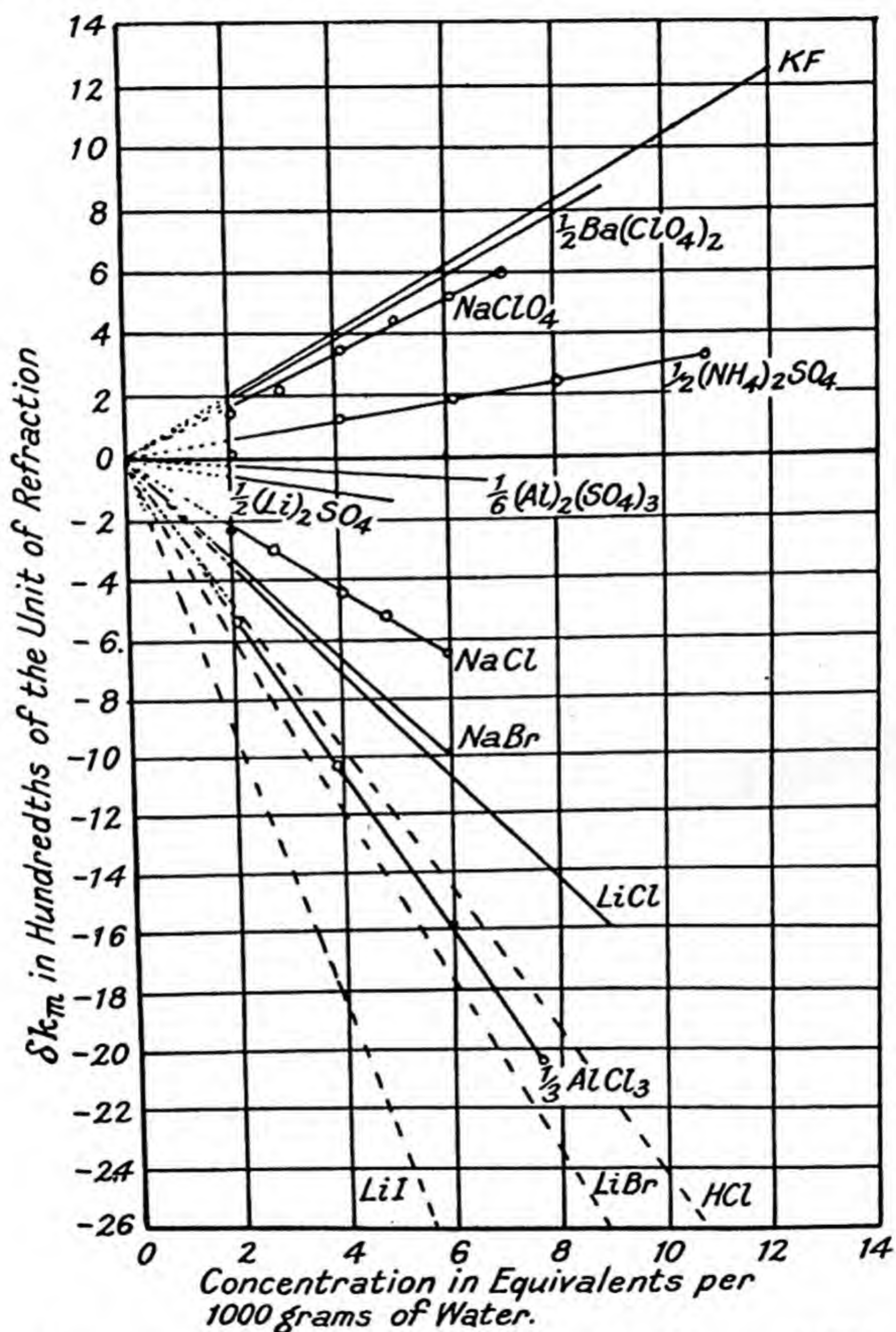


FIG. 19.—Variation of molecular refraction with concentration.

Fajans * has shown recently that for solutions of the sodium salts of a series of acids, including hydrochloric, nitric, and

* *Zeits. phys. Chem.*, 137, 361 (1928).

TABLE XLVI.

MOLECULAR REFRACTIONS OF SALTS.

Salt	LiI	LiBr	$\frac{1}{3}\text{AlCl}_3$	HCl	LiCl	NaBr	NaCl
k_m^0	—	—	8.21	—	8.76	12.90	9.27
δk_m	— .240	— .140	— .13	— .120	— .088	— .083	— .053
Salt	$\frac{1}{2}\text{Li}_2\text{SO}_4$	$\frac{1}{3}\text{Al}_2(\text{SO}_4)_3$	$\frac{1}{2}(\text{NH}_4)_2\text{SO}_4$	NaClO_4	$\frac{1}{2}\text{Ba}(\text{ClO}_4)_2$	KF	
k_m^0	7.08	6.57	11.70	13.44	15.44	4.86	
δk_m	— .013	— .008	+ .015	+ .042	+ .050	+ .055	

sulphuric acids, the changes of refraction with concentration are similar, both as regards the sign and the relative amounts, to those of these acids which occur as the concentration passes from an infinitely dilute solution to one of homogeneous undissociated acid. The changes in the case of the acids are due to the formation of undissociated molecules, and hence, on parallel grounds, the change in the salt solutions must be attributed to the same cause.

Schreiner * has measured the refraction of trichloroacetic acid, its sodium and lithium salts and also of hydrochloric acid at 18° C. From these measurements he calculated the degree of dissociation, and compared the results with those calculated from conductance measurements. There was general agreement up to concentrations of 2 normal, but at higher concentrations the optical method gave the higher values. The molecular refraction of the trichloroacetic acid decreases as the concentration is increased, but that of its salts is constant. With hydrochloric acid and lithium chloride the refraction also decreases with concentration, but the relationship is not a linear one.

Another interesting additive optical property of electrolytes is that of light absorption, in which the absorption produced by an electrolyte, completely ionised, is the sum of the absorptions resulting from the two sets of ions. We should expect dilute solutions of all salts, containing a common ion, to possess the same colour. In general this is so, *i.e.*, all chromates are yellow, all cupric salts blue, and all manganous salts pink. If both sets of ions are "colourless," then the solution should also be colourless.

Ostwald † photographed, on the same plate, absorption bands produced by various solutions. When the solutions were

* *Zeits. phys. Chem.*, **133**, 420 (1928).

† *Ibid.*, **9**, 579 (1892).

dilute the various bands of the permanganates, for example, had the same wave-length. In fact the absorption spectra were identical if the solutions contained the same coloured ion in equivalent quantities, associated with different kations. In general, the spectra are independent of the nature of the kation, the deviations that do occur being attributed to secondary effects. Merton,* however, has pointed out that the absorption bands of permanganates are similar even when different solvents are employed, in some of which the degree of ionisation must be very small. From this it is concluded that the absorption is due chiefly to the manganous radical, ionisation having little effect.

Ostwald also found that in other cases the spectra of dilute solutions were identical, provided that the solutions contained the same coloured ion. It may be noted that this ion coloration effect is widely used in the indicator method, applied to the titration of acids and bases. Thus phenolphthalein in acid solution is feebly dissociated, and is therefore colourless, whereas its salts in solution are pink, due to the anion from the dissociated salt. A change from a non-dissociated state to a dissociated one is therefore indicated by this change in colour.

Under certain conditions salt solutions containing an optically active ion have similar rotatory power.† If the optically active ion combines with an inactive one to produce an inactive salt, solutions of equivalent quantities of different salts containing this active ion should possess the same rotatory power, provided that complete dissociation occurs within the solutions. Thus, with the quinic acid salts in a one-seventh normal solution the molecular rotations are,

K	Na	NH ₄	Ba	Sr	Mg
48.8°	48.9°	47.9°	46.6°	48.7°	47.8°

the molecular rotation of the one-seventh normal quinic acid solution being 43.4°. It is, however, only slightly dissociated.

Jahn ‡ measured the magnetic rotation of the plane of polarisation in several electrolytic solutions, subtracting from these results the rotation produced under identical conditions by the water alone. His results were as follows :—

* *Trans. Chem. Soc.*, **99**, 637 (1911).

† See Landolt, *Ber.*, **6**, 1073 (1873); and Oudemans, *Lieb. Ann.*, **197**, 48, 66 (1879); **209**, 38 (1881).

‡ *Wied. Ann.*, **43**, 280 (1891).

Salt. → ↓	Magnetic Rotation of Solution.			
	Cl.	Br.	I.	$\frac{1}{2}\text{SO}_4$
Na	5.36	9.19	18.46	1.77
K	5.66	9.36	18.95	1.79
$\frac{1}{2}\text{Ca}$	4.70	8.80	—	—
$\frac{1}{2}\text{Sr}$	4.86	9.08	—	—
$\frac{1}{2}\text{Ba}$	5.05	9.27	—	—
$\frac{1}{2}\text{Cd}$	5.89	9.85	20.45	2.58

The differences between the magnetic rotatory properties of the chloride and bromide ions are, therefore,

Na	K	$\frac{1}{2}\text{Ca}$	$\frac{1}{2}\text{Sr}$	$\frac{1}{2}\text{Ba}$	$\frac{1}{2}\text{Cd}$
3.83	3.70	4.10	4.22	4.22	3.96

These differences are fairly constant, from which we assume that the kation has little effect upon the magnetic rotation.

71. Other additive properties of electrolytes.—In addition to the various additive properties of electrolytes instanced in the previous section we find other examples where, if ionisation is complete, the difference between a physical property of a solution and that of the solvent is a function of the difference brought about by the ions; but if the electrolyte is not completely ionised, the effect produced by the undissociated molecules must be taken into account. Thus, if any property, such as density, is independent of any interaction between the ions and the unionised molecules, its numerical value may be expressed by means of the equation,

$$P = P_s + A(1 - \alpha)C + B\alpha C, \quad . \quad . \quad (100)$$

where P and P_s are the numerical values of the properties of the solution and solvent, respectively, C , the molecular concentration, α , the degree of ionisation, and A and B , constants relating to the unionised molecules and ions, respectively. Equation (100) may be written in the form,

$$\frac{\delta P}{\delta C} = A(1 - \alpha) + B\alpha,$$

so that δP is a linear function of α , and from known values of δP values of α may be determined.

Valson * calculated the values of the specific gravities of salt

* *Comptes Rendus*, 78, 411 (1874).

solutions from those of the components, and Groshans* discovered that the molecular volume of a dissolved salt was, in dilute solution, the sum of two constants, one determined only by the acid, and the other solely by the base. Again, as Heydweiller† has shown, the density of aqueous solutions may be represented by a relationship of the type expressed by equation (100).

Consider a salt such as potassium chloride which, in very dilute solution, is completely dissociated, unit volume of the solution containing the same number of potassium and chloride ions. From equation (100) we have

$$P_K = P_W + B_K C,$$

and

$$P_{Cl} = P_W + B_{Cl} C,$$

the suffixes referring to the two types of ions. For a sodium iodide solution of equal molal concentration, in which dissociation is complete,

$$P_{Na} = P_W + B_{Na} C,$$

and

$$P_I = P_W + B_I C,$$

so that

$$P_{KCl} - P_{KI} = C[B_K + B_{Cl} - B_K - B_I].$$

Similarly,

$$P_{NaCl} - P_{NaI} = C[B_{Na} + B_{Cl} - B_{Na} - B_I],$$

or

$$P_{KCl} - P_{KI} = P_{NaCl} - P_{NaI}. \quad (101)$$

Suppose that P here represents the value of the equivalent conductance, Λ_0 , of infinitely dilute electrolytic solutions, then equation (101) states that

$$\Lambda_{0(KCl)} - \Lambda_{0(KI)} = \Lambda_{0(NaCl)} - \Lambda_{0(NaI)},$$

a relationship discussed previously in connection with Kohlrausch's theory of the independent ionic migration; in fact we have assumed this independent action of the ions in deducing equation (101).

Again, if P refers to the volume changes that occur when one mole of salt is dissolved in water, Traube‡ has shown that with the salts, potassium chloride, potassium iodide, sodium chloride,

* *Wied. Ann.*, 20, 492 (1883).

† *Ann. d. Phys.*, 37, 739 (1912).

‡ *Zeits. anorg. Chem.*, 3, 11 (1893).

and sodium iodide dissolved in this way, the volume changes are,

KCl = 26.7		NaCl = 17.7
	Difference = 18.7	Difference = 18.4
KI = 45.4		NaI = 36.1

the difference in the volume changes being due to the different anions.

Further, we may consider the densities of solutions formed by these salts in water, the concentration in all cases being 0.2 normal. At this strength the specific gravities are, at 0° C.,

KCl = 1.09255		NaCl = 1.08325
	Difference = 0.13513	Difference = 0.13573
KI = 1.22768		NaI = 1.21898

These various examples show that if we know the numerical values of a property of equally concentrated solutions of four salts represented by M_1X_1 , M_2X_2 , M_1X_2 and M_2X_1 , then these values conform to the relation

$$M_1X_1 - M_1X_2 = M_2X_1 - M_2X_2.$$

There is another important method by which the additive properties may be expressed, namely, by means of *moduli*. These were developed by Valson * who chose for his starting-point the densities of ammonium chloride aqueous solutions, *viz.*,

Concentration	N	2N	3N	4N	5N
Density at 18° C.	1.0157	1.0308	1.0451	1.0587	1.0728

Denoting the density of an n normal solution of this salt by ρ_n he showed that ρ , the density of an n normal solution of the salt MX, is given by

$$\rho = \rho_n + n(a + b),$$

where a and b are the differences between the density of a normal solution of ammonium chloride and that of normal solutions of salts represented by MCl and NH_4X , respectively, M and X being any metallic and acid radicals. The values of a and b , known as the *moduli* of the respective ions to which they refer, are determined experimentally. The moduli of different ions are as follows :—

* *Comptes Rendus*, 73, 441 (1871); 77, 806 (1873).

Ion Modulus $\times 10^4$	\cdot	\cdot	NH ₄ 0	K 289	Na 238	Li 78	$\frac{1}{2}$ Ba 735	$\frac{1}{2}$ Sr 500	$\frac{1}{2}$ Ca 280
Ion Modulus $\times 10^4$	\cdot	\cdot	$\frac{1}{2}$ Mg 210	$\frac{1}{2}$ Zn 410	$\frac{1}{2}$ Cd 606	$\frac{1}{2}$ Pb 1087	$\frac{1}{2}$ Cu 434	Ag 1061	H 16
Ion Modulus $\times 10^4$	\cdot	\cdot	Cl 0	Br 373	I 733	NO ₃ 163	$\frac{1}{2}$ SO ₄ 206	C ₂ H ₃ O ₂ — 15	OH 20

The density of a 3-normal aqueous solution of calcium bromide, calculated by means of these moduli, would be equal to ρ , where

$$\rho = 1.0451 + 3(280 + 373)10^{-4} = 1.2397.$$

This agrees well with the experimentally determined value, 1.2395. The moduli may be used to calculate the densities of very concentrated solutions, but the agreement between the calculated and experimental values is not always as close as that in the above example.

72. Diffusion.—Closely connected with osmosis is the phenomenon of *diffusion*. If two fluids in contact are able to mix in any proportions, they will do so spontaneously until a uniform mixture results. The process by which the inter-mixture is formed is called *diffusion*, and is produced by the molecular migratory movements which characterise fluids. Diffusion is comparatively slow with liquids, depending upon the rate of density change with distance at the place considered. It varies with the type of salt used, and increases both with concentration and temperature. These experimental results have been incorporated by Fick * in his law which states that, *if the concentration gradient, measured at right angles to a plane, is $\frac{dC}{dx}$, the mass of dissolved substance crossing unit area of this plane, per second, is equal to $D\frac{dC}{dx}$, where D is known as the coefficient of diffusion of the solute.*

If we consider unit area of two such planes, separated by a distance δx , and if C is the concentration of the solute in moles per c.c. at one plane, at any time t , then $C - \frac{dC}{dx}\delta x$ will be the concentration at the other plane. Thus by Fick's law, the amount of solute inflowing across the first plane, during a time δt , will be $D\frac{dC}{dx}\delta t$, while the outflow across the other plane during the

* Pogg. Ann., 94, 59 (1855).

same time interval will be $D \frac{dC}{dx} \delta t - D \frac{d^2C}{dx^2} \delta x \delta t$, so that the solute accumulates within the space between these planes at a rate equal to $D \frac{d^2C}{dx^2} \delta x$ per second. But this rate of accumulation may also be expressed in the form $\frac{dC}{dt}$, and thus,

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2}.$$

Consider a vertical cylinder of cross-sectional area A containing a non-electrolytic solution in the lower portion and water in the upper part. The solute gradually diffuses upwards until a uniformly concentrated solution results. Let the osmotic pressure at a height x within the cylinder be P , so that the upward force acting upon a thickness δx of the solution is $A\delta P$, where δP is the change in the osmotic pressure over the distance δx . Thus the upward force acting in the x direction upon each mole within this layer is equal to

$$-\frac{A\delta P}{CA\delta x}, \text{ or } -\frac{1}{C} \frac{dP}{dx},$$

the negative sign being introduced since the force is opposed to the osmotic pressure gradient. When steady motion is attained, the force f necessary to drive one mole of solute through the solution with unit velocity—1 cm. per sec.—is equal and opposite to the viscous drag exerted on this mole, and thus the velocity acquired by each mole is

$$-\frac{1}{f} \cdot \frac{1}{C} \frac{dP}{dx}.$$

Hence the number, δN , of moles of solute which cross area A in a time δt is given by

$$\delta N = -\frac{1}{fC} \frac{dP}{dx} \cdot CA\delta t = -\frac{A}{f} \cdot \frac{dP}{dx} \delta t.$$

Assuming that the solution is ideal, and that it obeys the perfect gas laws,

$$P = CRT,$$

so that

$$\delta N = -\frac{A}{f} \cdot RT \frac{dC}{dx} \delta t.$$

But by Fick's law,

$$\delta N = - \mathbf{D} A \frac{dC}{dx} \delta t, \quad . \quad . \quad . \quad (102)$$

and hence \mathbf{D} , the diffusion coefficient, is given by $\frac{RT}{f}$.

73. Diffusion in electrolytic solutions.—Diffusion occurs within an electrolytic solution as in any other solution, provided that a concentration gradient exists within it, but in addition to the osmotic pressure, we have to consider electrical forces. With an aqueous hydrochloric acid solution, for example, the hydrogen ions travel faster than the chloride ions and an electric field is set up, the more concentrated parts of the solution becoming *negatively* charged. This electrostatic field accelerates the slower moving chlorine ions and retards the more rapidly moving hydrogen ions, until the rates of movement become equal. Since separation of the ions does actually occur, an electrical potential gradient is established within the solution.

This process becomes more complicated when two different electrolytic solutions are in contact. For example, in the case of an aqueous hydrochloric acid solution, placed in contact with one of sodium chloride, since the chloride ions possess greater mobility than the sodium ions, more chloride ions than sodium ions from the sodium chloride solution pass into the hydrochloric acid solution, and, *vice versa*, more hydrogen ions than chloride ions move into the sodium chloride solution. Both effects, therefore, tend to make the latter *positive* with respect to the *acid* solution.

Consider an electrolytic solution in contact with pure water, such that one mole of the electrolyte yields on complete dissociation n_K gram kations, of valency ν_K and n_A gram anions, of valency ν_A . If P_K and P_A refer to the osmotic pressures exerted by the kations and anions, respectively, then,

$$P_K = n_K CRT; \quad P_A = n_A CRT,$$

where C is the concentration. The force acting upon the ions, contained within a slab of the solution of thickness δx and cross-sectional area A , is equal to

$$- \left(\frac{dP_K}{dx} + \frac{dP_A}{dx} \right) A \delta x = - (n_K + n_A) RT \frac{dC}{dx} \cdot A \delta x.$$

But this volume of solution contains $(n_K + n_A)CA\delta x$ gram ions,

and therefore the force due to osmosis, acting upon each gram ion, is given by

$$-\frac{RT}{C} \frac{dC}{dx}.$$

When steady conditions are reached, let $\frac{dE}{dx}$ be the resulting electrical potential gradient, so that the forces acting on one gram kation and anion are $-\nu_K F \frac{dE}{dx}$ and $+\nu_A F \frac{dE}{dx}$, respectively.

Thus the total force acting upon one gram ion is

$$-\frac{RT}{C} \cdot \frac{dC}{dx} - \nu_K F \frac{dE}{dx} \text{ for the kations,}$$

and
$$-\frac{RT}{C} \cdot \frac{dC}{dx} + \nu_A F \frac{dE}{dx} \text{ for the anions.}$$

If u_K' and u_A' represent the resulting velocities of the kations and anions, respectively, per unit force, the number, δN_K , of kations, and, δN_A , of anions which pass across the area A in a time interval δt are given by

$$\delta N_K = -u_K' n_K C A \left[\frac{RT}{C} \cdot \frac{dC}{dx} + \nu_K F \frac{dE}{dx} \right] \delta t,$$

and
$$\delta N_A = -u_A' n_A C A \left[\frac{RT}{C} \cdot \frac{dC}{dx} - \nu_A F \frac{dE}{dx} \right] \delta t.$$

But in order that there shall be no collection of free electricity in any part of the solution, equivalent quantities of the two ions must pass across any section in the same time, so that

$$\frac{\delta N_K}{n_K} = \frac{\delta N_A}{n_A},$$

$$\text{i.e., } u_K' \left[\frac{RT}{C} \cdot \frac{dC}{dx} + \nu_K F \frac{dE}{dx} \right] = u_A' \left[\frac{RT}{C} \cdot \frac{dC}{dx} - \nu_A F \frac{dE}{dx} \right],$$

or
$$F \frac{dE}{dx} = - \left(\frac{u_K' - u_A'}{u_K' \nu_K + u_A' \nu_A} \right) \frac{RT}{C} \cdot \frac{dC}{dx}.$$

Hence,

$$\delta N = \frac{\delta N_K}{n_K} = \frac{\delta N_A}{n_A} = - \left[\frac{u_K' u_A' (\nu_K + \nu_A)}{u_K' \nu_K + u_A' \nu_A} \right] A R T \frac{dC}{dx} \delta t \quad (103)$$

where δN is the number of moles of solute passing the section in time δt . Thus, comparing equations (102) and (103),

$$D = \left[\frac{u_K' u_A' (\nu_K + \nu_A)}{u_K' \nu_K + u_A' \nu_A} \right] R T.$$

If U_A and U_K are the velocities generated when unit force acts upon one gram-equivalent of ions, then

$$U_A = u_A' \nu_A \text{ and } U_K = u_K' \nu_K,$$

so that

$$D = \frac{U_K U_A}{U_K + U_A} \left[\frac{1}{\nu_K} + \frac{1}{\nu_A} \right] RT.$$

For uni-univalent electrolytes $\nu_K = \nu_A = 1$, and

$$D = 2 \frac{U_K U_A}{U_K + U_A} RT. \quad . \quad . \quad . \quad (104)$$

Thus if U_K and U_A are known, the coefficient of diffusion, D , may be calculated.

To illustrate the agreement between the calculated and experimentally determined values of D , let us consider the case of sodium chloride, in which the equivalent conductances of the sodium and chloride ions, at infinite dilution and 18°C. , are 43.48 and 65.54, respectively. The actual velocities, expressed in cms. per sec., of these ions when subjected to an electrical potential gradient of one volt per cm. are, therefore, $\frac{43.48}{96,491}$ and $\frac{65.54}{96,491}$, respectively. But this gradient gives rise to a force equal to $9,649.1 \times 10^8$ dynes, acting upon each gram-ion of the sodium and chloride ions, so that

$$U_K = u_K' = \frac{43.48}{(96,491)^2 \times 10^7} = 4.67 \times 10^{-16} \text{ cm. per sec.,}$$

and

$$U_A = u_A' = \frac{65.54}{(96,491)^2 \times 10^7} = 7.04 \times 10^{-16} \text{ cm. per sec.}$$

Thus taking $R = 8.315 \times 10^7$ ergs per mole, and the second as the unit of time, the diffusion coefficient of sodium chloride in very dilute solutions, at 18°C. , is equal to 1.358×10^{-5} C.G.S. units. For convenience, however, the day is taken as the time unit, so that in this case the value of the diffusion coefficient becomes 1.174, which agrees very well with that determined experimentally at a concentration 0.01 normal, namely, 1.170.

It has been assumed, so far, that the solute is completely ionised in solution. If this is not the case the neutral molecules will also diffuse, but at a rate which is, in general, different from that of the ions; usually their diffusion coefficient is less. Haskell,*

* *Phys. Rev.*, 27, 145 (1908).

working with 0.1 normal solutions of thallium sulphate and barium nitrate, found that the diffusion rate of the undissociated molecules was only one half that of the ions, and from this we conclude that the viscous drag acting upon the molecules is double that encountered by the ions.

Some of the values of the diffusion coefficients, determined experimentally for various electrolytes in water, are given in Table XLVII.* In these measurements the second is taken as the time unit.

TABLE XLVII.

DIFFUSION COEFFICIENTS OF ELECTROLYTES IN WATER AT 18° C.

Strength of Solution. Gram. Equivalents per Litre.	Diffusion Coefficient, $D \times 10^5$ C.G.S. Units.					
	KCl.	NaCl	KNO ₃ .	KOH.	LiCl.	CH ₃ COOH.
0.05	1.55	1.26	1.45	2.17	1.12	1.04
0.10	1.52	1.24	1.43	2.15	1.10	1.03
0.20	1.50	1.22	1.39	2.13	—	1.00
0.40	1.50	1.20	1.34	2.13	—	1.00
0.60	1.53	1.21	1.30	2.14	1.06	1.00
0.80	1.55	1.22	1.27	2.14	—	0.99
1.0	1.58	1.23	1.24	2.15	1.07	0.97
1.5	1.65	1.26	1.19	2.17	—	—
2.0	1.74	1.29	1.15	2.20	1.07	—
2.5	1.83	1.33	1.17	—	—	—
3.0	1.93	1.36	—	—	—	—
3.5	2.03	1.39	—	—	—	—
4.0	2.13	1.43	—	—	1.11	—
4.5	—	1.46	—	—	—	—
5.0	—	1.49	—	—	—	—

From these results it will be observed that those electrolytes which have the greater conductances also possess the higher diffusion coefficients, while in certain cases the diffusion coefficient actually increases with concentration. This fact may be partly explained on the solvation theory. As the concentration is raised, the number of solvent molecules attached to an ion decreases so that the ionic velocity is increased.

The diffusion coefficient of an electrolyte, diffusing into another electrolyte, is greater than when diffusion takes place into pure water, the electric potential gradient set up within the solutions, owing to the different velocities of the constituent ions, accelerating the diffusion process. Thus Arrhenius † found that a 1.04

* See Clack, *Proc. Phys. Soc.*, 36, 331 (1923); Ohölm, *Zeits. phys. Chem.*, 50, 309 (1904).

† *Ibid.*, 10, 51 (1892).

normal solution of hydrochloric acid, diffusing into water, had, at 12° C., a diffusion coefficient equal to 2.09, whereas when it diffused into a 0.085 normal potassium chloride solution, the coefficient was 2.51, and became still greater as the strength of the potassium chloride was raised. Some of his results for the inter-diffusion of different electrolytes at 12° C. are given in Table XLVIII. The day is the unit of time.

TABLE XLVIII.

DIFFUSION COEFFICIENTS OF ELECTROLYTES DIFFUSING INTO OTHER ELECTROLYTES.

Diffusing Electrolyte (A).	Electrolyte into which (A) Diffuses.	Diffusion Coefficient of (A).
1.04N HCl	Water.	2.09
"	0.75N KCl	4.22
"	0.028N KCl	2.27
"	0.1N NaCl	2.50
"	0.67N NaCl	3.51
"	0.085N BaCl ₂	2.46
"	0.75N BaCl ₂	4.12
0.55N HNO ₃	Water.	1.91
"	0.1N KNO ₃	2.59
"	0.5N KNO ₃	3.70
0.49N KOH	Water.	1.70
"	0.05N KNO ₃	1.91
"	0.5N KNO ₃	2.54
"	0.5N KCl	2.57

Nernst,* on theoretical grounds, considered that the relation between the diffusion coefficient and temperature could be expressed by means of the formula,

$$D_t = D_{18}[1 + \beta(t - 18)],$$

where D_t and D_{18} are the values of the diffusion coefficients at t° C. and 18° C., respectively, and β is the diffusion temperature coefficient. For most neutral salts $\beta = 0.026$, and Ohölm † found that its value for different electrolytes increased, as the value of the diffusion coefficient decreased. He concluded that β was equal to the sum of the temperature coefficients of osmotic pressure and electrical conductivity. The values of D , as determined by Stiles, ‡ for normal solutions in gels at different temperatures, are shown in Table XLIX. :—

* *Zeits. phys. Chem.*, 2, 613 (1888).

† *Proc. Roy. Soc., A*, 103, 260 (1923).

‡ *Loc. cit.*

TABLE XLIX.

DIFFUSION COEFFICIENTS AT DIFFERENT TEMPERATURES.

Salt.	Diffusion Coefficient, $D \times 10^5$ C.G.S. Units.			
	0° C.	20° C.	30° C.	40° C.
NH ₄ Cl	0.93	1.63	2.07	2.49
LiCl	0.70	1.24	1.58	1.93
KCl	0.94	1.64	2.07	2.50
NaCl	0.78	1.39	1.77	2.20
CaCl ₂	0.65	1.16	1.48	1.83
BaCl ₂	0.66	1.16	1.48	1.80
MgCl ₂	0.61	1.12	1.42	1.73

BIBLIOGRAPHY.

- Auwvers, Zeits. phys. Chem., **42**, 513 (1903).
 Bancroft and Davis, Jour. Phys. Chem., **32**, 1 (1928).
 Barth, Zeits. Wiss. Phot., **24**, 158 (1926).
 Beckmann, Zeits. phys. Chem., **2**, 715 (1888).
 Brönsted, Jour. Amer. Chem. Soc., **44**, 877 (1922).
 Chéneveau, Comptes Rendus, **172**, 1408 (1921); **174**, 815 (1922).
 Cuthbertson, Proc. Roy. Soc., A, **114**, 659 (1927).
 Dieterici, Ann. d. Phys., **70**, 558 (1923).
 Flugel, Zeits. phys. Chem., **79**, 577 (1912).
 Godlewski, Jour. Chim. Phys., **3**, 393 (1905).
 Hantzsch, Zeits. phys. Chem., **86**, 624 (1914).
 Hausrath, Ann. d. Phys., **9**, 522 (1902).
 Jahn, Zeits. phys. Chem., **59**, 31 (1907).
 Limann, Zeits. f. Phys., **8**, 13 (1921).
 MacInnes, Jour. Amer. Chem. Soc., **48**, 2068 (1926).
 Neale, Trans. Farad. Soc., **17**, 505 (1921).
 Osaka, Zeits. phys. Chem., **41**, 560 (1902).
 Paterno, Ber., **22**, 1430 (1889).
 Peterson and Rodebush, Jour. Phys. Chem., **32**, 709 (1928).
 Randall and Scott, Jour. Amer. Chem. Soc., **49**, 647 (1927).
 Randall and Vanselow, *ibid.*, **46**, 2418 (1924).
 Reyher, Zeits. phys. Chem., **2**, 744 (1888).
 Röntgen and Schneider, Wied. Ann., **34**, 531 (1888).
 Rozsa, Zeits. Elektroc., **17**, 934 (1911).
 Schreber, *ibid.*, **32**, 149 (1926).
 Smits, Proc. Acad. Sci. Amsterdam, **19**, 708 (1917).
 Walden, Zeits. phys. Chem., **59**, 192 (1907).
 Whetham, Theory of Solutions.
 Wiedemann, Pogg. Ann., **135**, 177 (1868).

CHAPTER VI.

CELLS AND ELECTROMOTIVE FORCE.

74. Introduction.—In the preceding chapters we have dealt with the dissociation theory as applied to electrolytes, and by means of it we developed the laws which regulate the equilibrium of homogeneous electrolytic solutions. We now pass on to consider the free energy reactions that occur when an electrolyte passes from one dilution to another, and, in particular, we shall study the case where the ions are removed from one solution to another and are separated at the electrodes.

According to Nernst* a metal possesses a tendency to pass into solution, the so-called *characteristic solution pressure*, comparable, for example, with the vapour pressure of a liquid, and if a metal rod is placed in water, metal ions carrying their positive charge of electricity pass from the metal into the liquid, the metal thus becoming negatively charged. As a result, a *double layer of electrical charge* is established at the metal-solution interface, and since the potential difference thus set up opposes further solution of the ions, equilibrium is finally established. On the other hand, the metallic ions now in the solution exert osmotic pressure, and are deposited upon the metal which, therefore, receives the positive charge associated with the metallic ions. Thus the true equilibrium state is attained when the tendencies of the metal ions to pass to and from the liquid are equal. The osmotic pressure is proportional to the ionic concentration but, in general, is not equal to the solution pressure, so that on the whole the metal receives a net electrical charge, the sign of which is positive, or negative, according as the osmotic pressure is greater or less than the solution pressure. The potential difference thus set up prevents further deposition, or solution, and equilibrium is attained.

Although the Nernst conception accounts for the potential differences exhibited by metals when immersed in solutions of their salts, its adequacy has been disputed by many. The solution pressure of a metal, if such exists, depends not only on the metal,

* *Zeits. phys. Chem.*, 2, 613 (1888); 4, 129 (1889).

but also upon the solvent in which it dips, since it has been shown that the potential difference between metal and solution varies for the same metal in different solvents. It is difficult to imagine why an expansive force (solution pressure) within a metal should vary with the surrounding medium when the external force (osmotic pressure) is kept constant, or why it should not be effective when the metal is surrounded by air. But we obtain what seems to be conclusive evidence against the solution pressure theory by making a simple computation, either of the speed with which an ion would have to leave the surface of a magnesium electrode in water, even on the assumption that the solution pressure acts only through a molecular distance, or of the mass of the ions which a magnesium electrode would need to lose in water in order that the solution pressure may be balanced by the sum of the osmotic pressure and the electrostatic attraction. Both of these calculations give values which are not only absurd but impossible, the speed of the ion in the first case being greater than the velocity of light, and the mass of ions lost in the second case being such that the density of the solution would be greater than that of the metal.*

Ulrey suggested that taking into account the specific inductive capacity of the electrolyte does away with the necessity of the employment both of osmotic pressure and solution pressure. The transfer of ions between the metal and the electrolyte, he supposes, is brought about by electrical forces, the magnitude of which must depend, other things being equal, upon the specific inductive capacity of the medium. On the other hand, it is possible that in addition to the metal ions, electrons may pass from the metal into the liquid, and consequently the laws of dilute solutions should be applied to electrons within the electrolyte.† Kleeman ‡ suggested that there is a transition layer present at the metal surface, produced owing to the difference between the diffusion velocities of the positive and negative ions. The potential difference at the metal-liquid interface then results from a segregation of ions within this layer, and the tendency of the metal to pass into solution is a purely secondary effect as regards the production of this potential difference.

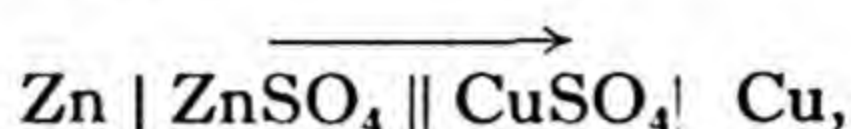
Whatever the exact nature of the process, a potential difference undoubtedly exists, and if two metallic conductors are placed in an electrolytic solution, an electric current will flow along a wire connecting them, provided that some difference exists

* See Ulrey, *Phys. Rev.*, 12, 47 (1918).

† See Smits, *The Theory of Allotropy*.

‡ *Phys. Rev.*, 20, 174 (1922).

between the nature of the metals constituting the conductors, or between the electrolytes which are in immediate contact with them. Thus a potential difference between the two conductors is created under any one, or more, of the following conditions : (a) two different metals in the same electrolyte ; (b) two different metals in different electrolytes ; (c) the same metal in different electrolytes ; (d) the same metal in a solution of the same electrolyte, the latter being at two different concentrations. For example, in a Daniell cell,



the zinc sends zinc ions into the solution to some extent, thereby becoming negatively charged, and some copper ions tend to precipitate upon the copper plate, charging the latter positively. The current flows, outside the cell, from the copper to the zinc, and, inside, from the zinc through the solution to the copper.* Now the chemical potential energy of zinc is higher than that of copper, and since the electromotive force is a measure of the difference between chemical potentials, it seems necessary to say that the zinc electrode is the place of high electrical potential and the copper electrode that of low electrical potential, in which case one must concentrate on the direction of the current through the solutions. On this basis the potential difference at the $\text{Zn} \mid \text{ZnSO}_4$ interface would be given the positive sign. Ostwald † and Nernst ‡ both used the positive sign for zinc.

In connection with the sign to be given to any particular electrode, it is interesting to note that Gibbs § considered the electromotive force of a cell as being equal to the difference in the values of the chemical potential of any ion, or apparent ion, at the electrode surfaces, multiplied by the electro-chemical equivalent of that ion, the greater chemical potential of a kation being at the same electrode as the greater electrical potential, and the reverse being true of an anion. This means || that when zinc ions go into solution at the zinc electrode, the decrease in the chemical potential of the zinc raises the electrical potential

* In representing a voltaic cell, or a voltaic element such as $\text{CuSO}_4 \mid \text{Cu}$, the positive electrode throughout this work will be on the right. A single vertical line indicates a metal-liquid interface, and a double vertical line, a liquid-liquid junction. In many cases a horizontal line will be drawn, the direction in which the arrow points representing the direction of the flow of *positive* electricity *inside* the cell.

† *Zeits. phys. Chem.*, **1**, 604 (1887).

‡ *Zeits. Elektrochem.*, **7**, 254 (1900).

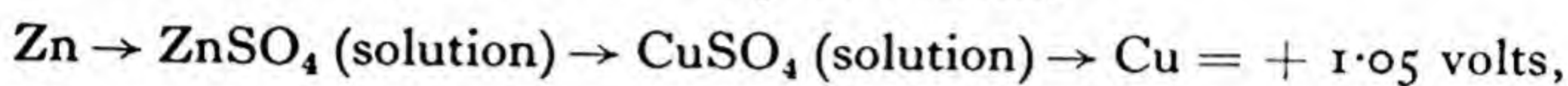
§ *Scientific Papers*, **1**, 333 (1906).

|| See Bancroft, *Trans. Amer. Electrochem. Soc.*, **33**, 79 (1918).

of the solution, and that the copper ions deposited upon the copper increase the electrical potential of this metal.

While the electromotive force of the cell is generated practically entirely at the two metal-solution interfaces, it is balanced by the differences of the chemical potentials which give rise to the potential differences at these interfaces, and consequently it is only when the circuit is closed that we get equilibrium disturbed, the current passing outside the cell from the copper to the zinc.

The equation of the cell may be written,



showing that there is a gain of electrical potential when the electric displacement is from the left to right along the path indicated. In this way we represent the current as rising in potential on the whole in passing from the zinc to the copper through the cell. Further, we know that the zinc sulphate solution is positive to the zinc metal, while the copper sulphate solution is negative to the copper. Thus there is a decrease in the free energy in each of the steps from left to right as well as a decrease on the whole. If the internal and free energies of a system increase we must regard these changes of energy as positive, *e.g.*, there is an energy gain when a liquid evaporates, and this gain, which is equal to the internal latent heat, must be taken as positive. In a similar manner the energy gain in a chemical reaction must also be taken as positive.

As regards the action of the Daniell cell, we can only say at present that some of the zinc goes into solution, carrying a positive charge with it. This process is one not merely of evaporation, as in the Nernst theory, but is, in part, assisted by the SO_4^{--} ions which attract the Zn^{++} ions. Again, copper is deposited at the copper plate, not freely as a vapour might condense, since it is retarded by the attractions of the SO_4^{--} ions in the solution.*

75. Reversible and Non-reversible Cells.—As a result of the chemical reactions that occur within the Daniell cell one gram-equivalent of zinc is dissolved, and an equivalent amount of copper deposited at the appropriate electrodes, when one faraday of electrical charge is taken from the cell, and, therefore, we should expect that under suitable conditions these chemical reactions would be completely reversed by passing one faraday *through*

* See Porter, B.A., Section A (1928).

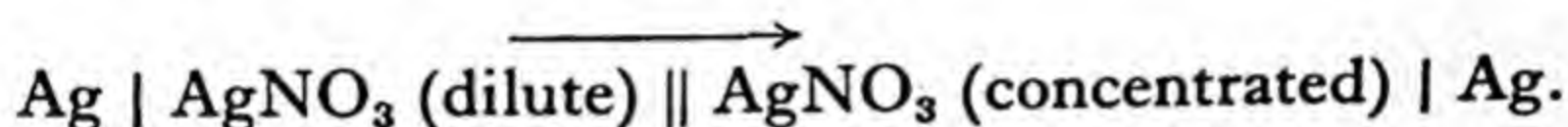
the cell from the copper to the zinc electrodes. We can imagine a reversible system composed of the cell and some source of opposing electromotive force, the latter being equal in value to that of the cell. Under these circumstances no chemical actions occur, but if the electromotive forces differ, even by an extremely small amount, electricity flows from or into the cell, the direction of flow being determined by the relative values of the two electromotive forces. Such a cell is said to be *reversible*. Within it there are no irreversible processes, such as the liberation of gas, production of heat, diffusion of ions and other similar effects.

We may classify reversible voltaic cells into the following types :—

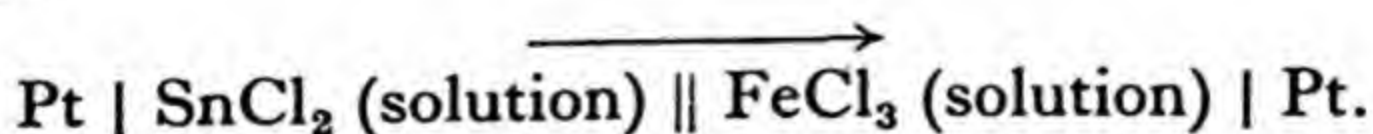
(a) *Chemical cells*, in which chemical reactions are involved. The Daniell cell already discussed is an example of this class.

(b) *Accumulators*. In these cells the chemical energy contents are first increased by passing electricity into them, this increased energy being afterwards recovered as electrical energy. The ordinary lead accumulator is the best-known example of this type.

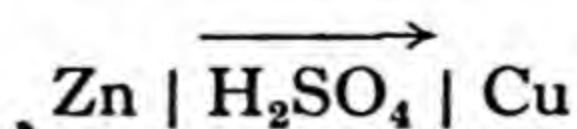
(c) *Concentration cells*. They consist of electrodes of the same metal dipping into electrolytic solutions of different concentrations and containing ions of the metal, *e.g.*,



(d) *Oxidation and reduction cells*. In this type the energy of oxidation and reduction processes, during which changes occur in the valency of the ions, can be made to supply an electric current, *e.g.*,



In all of the above types the cell may be restored to its original state, but with the simple Volta cell



zinc passes into solution and hydrogen separates at the copper electrode. If an electric current is sent through the cell from the copper to the zinc, copper is dissolved and hydrogen is again liberated, but at the zinc electrode. Under no conditions is the cell restored to its original state and it is said to be *non-reversible* or *irreversible*. An electromotive force, greater by an indefinitely small amount than the electromotive force of the cell, neither

reverses the direction of the current through it, nor the chemical reactions within it.

76. Calculation of the electromotive force of a reversible voltaic cell.—Thomson* calculated the electromotive force of a Daniell cell on the assumption that the work done by the cell in maintaining the current is equal to the energy liberated when one gram-equivalent of zinc is dissolved and an equivalent amount of copper deposited, this energy being determined by means of calorimetry experiments. The value obtained, 1.086 volts, agreed closely with observed values. The method of calculating the electro-motive force of a reversible voltaic cell is as follows:—

Since the Gibbs-Helmholtz equation of free energy, equation (5), is a linear one, it may be written in the form,

$$\delta\psi = \delta E + T \frac{\partial}{\partial T}(\delta\psi). \quad . \quad . \quad . \quad (105)$$

Let \mathbf{E} be the E.M.F. of a reversible voltaic cell, and suppose that when N faradays of electricity pass through the cell, one mole of metal goes into solution at one electrode, and one mole of another metal is deposited from the solution upon the second electrode. For example, in a Daniell cell, one mole of zinc enters the solution from the zinc electrode and one mole of copper is deposited upon the copper plate when two faradays pass. The change, $\delta\psi$, in the free energy is equal to $-NFE$, where \mathbf{E} is positive if free energy is evolved, *i.e.*, if the reaction is a spontaneous one. Hence from equation (105),

$$-NFE = \delta E - NFT \frac{\partial \mathbf{E}}{\partial T},$$

δE being the increase in the internal energy of the cell. This increase will be the same if the final state of the system is reached in any other way, as, for example, by direct chemical action, and the energy equivalent of this increase can be determined by measuring the heat absorbed by the reaction. Let H_v be this heat of reaction,† per mole, corresponding to the chemical changes which occur; then we obtain,

$$\mathbf{E} + \frac{H_v}{NF} = T \frac{\partial \mathbf{E}}{\partial T}. \quad . \quad . \quad . \quad (106)$$

* *Collected Papers*, 1, p. 250.

† If the heat is evolved then H_v is negative.

If E is expressed in volts, H_v in calories, and both metals are equi-valent, and of valency ν , then,

$$E = -\frac{4.18H_v}{\nu F} + T\frac{\partial E}{\partial T}. \quad (107)$$

It will be noted that, strictly speaking, this equation refers only to constant volume conditions, whereas a cell reaction occurs under constant pressure conditions. In general, however, the volume changes are, if any, very small.

Equation (107) may also be deduced with the aid of a Carnot cycle as follows:—

(a) Let A (Fig. 20) represent the initial state of the cell.

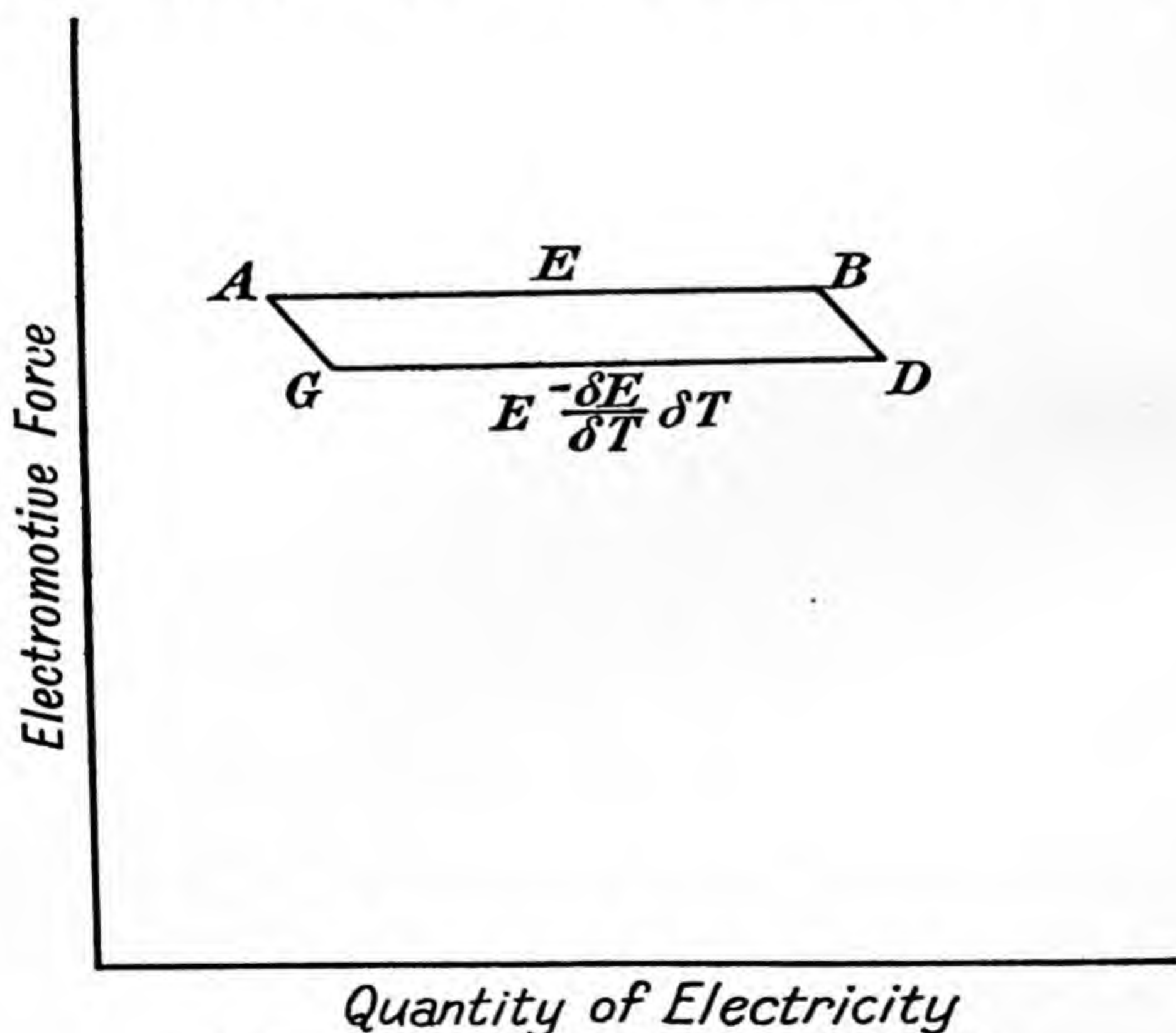


FIG. 20.—Electromotive force of a voltaic cell.

Allow it to generate ν faradays of electricity under isothermal conditions, during which heat equal to h is *absorbed* from the surroundings.

(b) Thermally isolate the cell and obtain from it a further quantity of electricity. Since during this operation, BD, no heat enters the cell, the electrical energy supplied must come from

the internal energy and therefore the temperature of the cell falls from T to $T - \delta T$, the electromotive force decreasing from \mathbf{E} to $\mathbf{E} - \frac{\partial \mathbf{E}}{\partial T} \delta T$.

(c) Connect the cell to an external source of electromotive force and, keeping the temperature constant at $T - \delta T$, pass ν faradays through it. This process is represented by DG.

(d) Finally, thermally isolate the cell and send a further small amount of electricity through it, so that the cell is restored to its original state.

This cycle is reversible, and therefore from Carnot's principle,

$$\frac{\nu F \mathbf{E} - \left(\mathbf{E} - \frac{\partial \mathbf{E}}{\partial T} \delta T \right) \nu F}{h} = \frac{\delta T}{T},$$

or
$$h = \nu F T \frac{\partial \mathbf{E}}{\partial T}.$$

If, as before, $-H_v$ is the heat of reaction, *i.e.*, heat evolved, and ν faradays are associated with the reaction, per mole, the *output* of electrical work during the first operation in the cycle is equal to $\nu F \mathbf{E}$, where

$$- \nu F \mathbf{E} + h = H_v,$$

or
$$- \nu F \mathbf{E} + \nu F T \frac{\partial \mathbf{E}}{\partial T} = H_v,$$

whence equation (107) follows immediately. Thus the electromotive force of a cell may be calculated from the heat of reaction that takes place within it. This result, which was first derived by Helmholtz,* has been tested by many workers. Cohen, Chattaway and Tombrock,† used the Daniell cell,



and at 15° C. they found the heat of reaction (evolved) per mole to be 55,189 gram-calories when measured by means of calorimetry experiments. Their electrical measurements gave

$$\mathbf{E}_{15} = 1.09337 \text{ volts and } \left(\frac{\partial \mathbf{E}}{\partial T} \right) = -0.000429,$$

so that $H_v = -56,089$ gram-calories.

From equation (106) it is evident that since, in general, $\frac{\partial \mathbf{E}}{\partial T}$ is not zero, the electrical energy obtained from a cell is not equiv-

* Sitz. Ber. Berlin Akad., 1, 22 (1882).

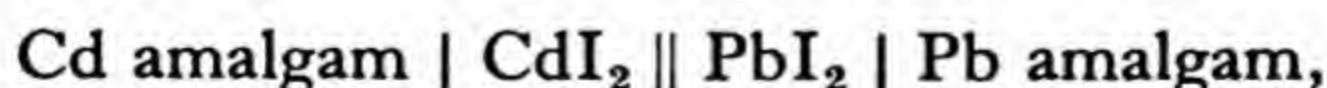
† Zeits. phys. Chem., 60, 706 (1910).

alent to the heat of reaction, but there is, in addition, a reversible evolution, or absorption, of heat energy within the cell equal, numerically, to $FT\frac{\partial E}{\partial T}$ per faraday. This reversible heat effect, which is not to be confused with the irreversible heat produced when the current passes through a resistance, the so-called Joule heating effect, has been determined for certain cells by Jahn.* His results are given in Table L. which also includes the values of the heat of reaction, H_v .

TABLE L.
HEATS OF REACTION.

Cells.	E.M.F. at 0° C. Volts.	$\frac{dE}{dT}$	H_v (Calories).		Reversible Heat Effect (Calories).	
			Observed.	Calculated.	Observed.	Calculated.
Zn ZnCl ₂ + 100H ₂ O AgCl Ag	1.031	- 0.000409	- 52,170	- 47,506	- 4,660	- 5,148
Zn ZnBr ₂ + 25H ₂ O AgBr Ag	0.841	- 0.000106	- 39,936	- 38,772	- 1,164	- 1,334
Cu Cu(NO ₃) ₂ + 100H ₂ O AgNO ₃ + 100H ₂ O Ag	0.458	+ 0.00071	- 21,120	- 30,040	+ 8,920	+ 8,920
Pb Pb(NO ₃) ₂ + 100H ₂ O AgNO ₃ + 100H ₂ O Ag	0.932	- 0.000629	- 50,870	- 42,980	- 7,950	- 7,890
Hg Hg ₂ O in 0.01N KOH Hg ₂ Cl ₂ in 0.01N KCl Hg	0.328	+ 0.0018	+ 3,820	+ 7,566	+ 11,386	+ 11,276

Hence the heat of reaction may be calculated from the experimentally determined value of the E.M.F. of any galvanic combination, and if the heat of reaction of one of the constituents is known, that of the other may be calculated. For example, Obata † measured the E.M.F. and temperature coefficients of cells of the type,



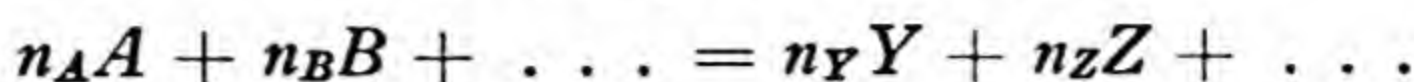
and from the results he determined the heats of formation of the cadmium haloid salts. The values thus obtained agreed with those found by means of thermo-chemical experiments.

The electromotive force of a cell may also be calculated in

* *Wied Ann.*, 28, 21 (1886).

† *Phys. Math. Soc., Japan Proc.*, 3, 136 (1921).

the following manner. Consider a cell such that, when ν faradays of electricity pass, a reaction represented by



occurs. From equation (32) we have

$$\delta\psi = \delta\psi_0 + RT \log \frac{C_Y^{n_Y} \cdot C_Z^{n_Z} \dots}{C_A^{n_A} \cdot C_B^{n_B} \dots}$$

But $\delta\psi = -\nu F \mathbf{E}$, and therefore,

$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{\nu F} \log \frac{C_Y^{n_Y} \cdot C_Z^{n_Z} \dots}{C_A^{n_A} \cdot C_B^{n_B} \dots}, \quad (108)$$

where \mathbf{E}_0 is the E.M.F. of the cell when each of the substances is in its standard state. Thus, in a lead accumulator,



the cell reaction is



and, if we express the concentration of a substance by the formula in square brackets,

$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{\nu F} \log \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2\text{SO}_4][\text{H}_2]},$$

since the concentrations of the solid substances remain the same. Hence the electromotive force varies with the composition of the solution.

We have also shown, equation (32), that

$$\delta\psi_0 = -RT \log K,$$

and since

$$\delta\psi_0 = -\nu F \mathbf{E}_0,$$

$$\mathbf{E}_0 = \frac{RT}{\nu F} \log K. \quad (109)$$

Noyes and Brann* formed ferrous nitrate and silver nitrate from the action of ferric nitrate on silver. From the measured concentrations of the Fe^{++} , Fe^{+++} and Ag^+ ions at the equilibrium state, they extrapolated to infinite dilution, and determined K_{298} to be 0.128, where

$$K_{298} = \frac{[\text{Fe}^{++}][\text{Ag}^+]}{[\text{Fe}^{+++}]}$$

* *Jour. Amer. Chem. Soc.*, **34**, 1016 (1912).

Since $\nu = 1$, we have from equation (109) that E_0 at 25°C. is equal to -0.0528 volt. This agrees with the value found from electromotive force measurements.

77. Calculation of the potential difference at a metal-solution interface.—We have seen, previously, that if a metal be placed in a solution of its salt, there will be a potential difference set up between the metal and solution which will vary with the concentration of the metal ions: the higher the concentration of the positive metallic ions in the solution the more positive will be the electrical charge on the metal, and, conversely, the lower the concentration of the metallic ions in the solution, the less positive will be the charge on the metal. Thus, as the osmotic pressure of the metal ions increases, the tendency of the metal to dissolve becomes less, and at a certain pressure no further tendency to dissolve exists. This critical pressure bears no relation to the limit set to the osmotic pressure of a solution by reason of the finite solubility of the salt. If the concentration of the solution exerting this critical pressure could be obtained, so that there would be no tendency for ions of the metal to enter, or leave, the liquid, we conclude that the metal and solution under these circumstances would be electrically neutral to each other, and that no potential difference would exist between them. The value of this critical osmotic pressure is taken as the electrolytic solution pressure of the metal in the given solution. From this point of view the potential difference, π , at a metal-solution interface may be calculated as follows:—

Let P be the osmotic pressure of the ions in solution, and p the solution pressure of the metal, and let us assume that the ions obey the ideal gas laws, an assumption that is unjustifiable. Now a thermodynamic cycle can be performed, at constant temperature, by passing a current reversibly across the interface from a balancing applied potential difference. Suppose that $P > p$, the metal being positive with respect to the solution, and let ν be the valency of the ions. Pass that quantity of positive electricity, which is associated with one gram-ion of the metal, from the metal to the solution. Electrical work will be done *by* the interface system equal to $\nu F \pi$ and there will be an *increase* in the number of metal ions in solution.

Assuming the volumes of the liquid and metal to be so great that the introduction, or withdrawal, of one gram-ion of metal does not change the osmotic pressure, or the solution pressure, respectively, let v_1 be the volume occupied by one gram-ion of the metallic ions which disappear at a pressure p , from the metal,

and appear at volume v_1 and pressure P , in the solution. Thus, the work done on the interlace system during this change is

$$\nu F\pi + Pv_2 - pv_1.$$

The interface can then be restored to its original condition by allowing the ions, which have appeared in the solution, to "expand" isothermally from v_2 to v_1 , and then adding them to the metal. The work done by the ions during this process is $\int_{v_2}^{v_1} p dv$.

In the complete cycle these operations are reversible and can be performed isothermally, so that the gain of energy by the system is zero, hence,

$$\nu F\pi + Pv_2 - pv_1 - \int_{v_2}^{v_1} p dv = 0.$$

Assuming the laws of an ideal gas to hold, and remembering that the temperature is constant,

$$Pv_2 = pv_1.$$

Hence,

$$\nu F\pi = \int_{v_2}^{v_1} p dv,$$

or

$$\nu F\pi = \int_{v_2}^{v_1} \frac{RT}{v} dv,$$

and we have

$$\pi = -\frac{RT}{\nu F} \log \frac{p}{P},$$

a result first obtained by Nernst.* If $p > P$ then the left-hand side of this equation is negative. In other words, free energy is lost and electrical energy is gained when π , the potential of the metal, is positive with respect to the solution. It will be more convenient if we refer to this gain in electrical energy, in which case

$$\pi = \frac{RT}{\nu F} \log \frac{P}{p}. \quad (110)$$

Since $F = 96,491$ coulombs, and $R = 8.32$ joules per mole, we have, at 18°C. ,

$$\pi \text{ (volts)} = \frac{0.058}{\nu} \log_{10} \frac{P}{p}, \quad (111)$$

from which it is evident that a ten-fold increase, or decrease, in the value of the osmotic pressure, is attended by an increase, or decrease, in π of $\frac{0.058}{\nu}$ volt.

* *Zeits. phys. Chem.*, 4, 150 (1889).

In solutions containing their own ions, the noble metals, such as gold, silver, copper, etc., acquire a positive potential, while metals like zinc, iron, nickel, etc., acquire a negative potential, so that the potential of a metal in contact with a solution containing its own ions is positive, or negative, according as P is $>$ or $< p$.

Metals which are positive to their solutions have a strong tendency to come out from the ionic form, and are therefore easily deposited, analytically, whereas if the metal has a strong tendency to form ions it becomes negatively charged, and is said to possess negative *electro-affinity*. An anode electrode which is positive to a solution of its ions has a strong tendency to form ions and the metal is difficult to liberate by means of electrolysis.

This theory of solution pressure, according to which each metal has a tendency to throw off positive ions into its environment, has been strongly criticised because it is extremely unlikely that positive ions in the metal are only retained there presumably by the slowness with which equilibrium is reached. In addition, when the experimentally determined values of π for different metals are compared with equation (110), it is found that enormous pressures for the alkali metals and extraordinarily small pressures for the noble metals must exist within the electrodes if the Nernst theory is true. Thus Leffeldt* found that the solution pressures, expressed in atmospheres, were, for zinc, nickel and palladium, 9.9×10^{18} , 1.3×10^0 and 1.5×10^{-36} , respectively, and in order to permit at the electrode the pressure indicated for palladium the solution would have to be so dilute as to contain but one or two palladium ions in a space the size of the earth. No stable potential could be measured under such circumstances. On the other hand, Leffeldt calculated that to produce the high pressure indicated for zinc 1.27 grams of the metal would have to pass into the ionic form per square centimetre, which is obviously impossible. This difficulty has thrown discredit on the Nernst theory, which has come to be regarded as only useful for the deduction of the logarithmic relationship.

The ions in solution do not obey the laws which hold for ideal gases. Porter† has shown that by taking the ions as following more nearly the law of a liquid, *i.e.*, v is constant,

$$\pi = \frac{v}{vF}(P - p).$$

Very much smaller values of p now correspond to a given experimental electromotive force. Without going as far as this, we can

* *Phil. Mag.*, 48, 430 (1899).

† *Trans. Farad. Soc.*, 19, 817 (1924).

adjust to the invalidity of the perfect gas laws by assuming another relationship which more nearly represents the behaviour of a gas. For example, we might employ van der Waal's equation, simplified to

$$P = \frac{RT}{v - b}.$$

Substituting this value in the equation

$$\nu F d\pi = \nu dP,$$

and integrating the result, we get

$$\pi = \frac{1}{\nu F} \left\{ b(P - p) + RT \log \frac{P}{p} \right\},$$

where b is a constant. This result again leads to more moderate values of p .

78. Theories of the electrode potential.—The failure of the Nernst hypothesis has led investigators to consider other possible explanations of the metal-solution interface potential difference, and one of the most interesting theories is that which introduces the idea of the true Volta or contact potential difference. If two dissimilar metals are placed in contact, a potential difference is set up, and Volta maintained that the electromotive force of a cell had its seat in the contact potential difference between the metals and their respective electrolytes.

Now electrons within atoms may be abstracted by various means, such as heating the metal or allowing ultra-violet rays to fall upon it, and the greater the retaining power of the atom for the electron, the more energy must the atom receive before the electron is liberated. This affinity of metals for electrons is termed *electron affinity*, ϕ , and its value can be calculated in volts for different metals, either by measuring the thermionic, or the photoelectric, emission from metals.* There is, in general, a difference in the values of ϕ for different metals, so that if two metal bars or strips are placed in a vacuum, the electrons will be drawn from the metal of lower electron affinity, and a difference in potential, $\pi_A - \pi_B$, will occur between the metals, where $\pi_A - \pi_B = \phi_A - \phi_B$. The metals must have perfectly clean surfaces, and it is for this reason that they are placed in a vacuum.

If the values of ϕ for different metals are arranged in order of magnitude, a series is obtained which is very much the same

* See Richardson, *Thermionics*, and Allen, *Photoelectricity*.

as the ordinary electromotive order,* and it appears that there is some relationship between the electron affinity of a metal and its position in the electromotive series, but the fact that the potential differences existing at metal-solution interfaces are dependent upon the concentrations of the electrolytes concerned rules out the possibility of interpreting electrode-potential differences solely by reference to a quantity, which might otherwise be adequate to account for the Volta effect.

On the assumption that the electromotive behaviour of metals is mainly determined by their electron affinities, Rideal † has derived a thermodynamic formula for the E.M.F. of a cell of the Daniell type, which reduces to the accepted form, when applied to concentration cells. It leads to the conclusion that the difference between the electrode-potential and the electron affinity of the metal is dependent upon the atomic volume of the latter. In so far as the relation can be tested, it appears to receive some support from the available data.

Kleeman ‡ supposed that the layer of solution adjacent to the metal plate is different from the rest of the solution in density, concentration of solute and in degree of dissociation; and because of the difference between the diffusion velocities of the positive and negative ions, a segregation of the ions results which produces an electric field through the layer, and also charges the plate and the solution oppositely. These two fields, one due to the asymmetrical distribution of ions and the other due to the charge on the plate, together cause the potential difference observed between the metal and the solution.

If the concentration of the metal ions in solution is less than corresponds to equilibrium, metal ions will leave the surface of the metal and pass into solution, thereby leaving the former with an excess of negative electrons, since it is generally agreed that metals are largely ionised into positive ions and free electrons. The effect of the negative charge is to retard the passage of positive ions away from the surface and to assist their deposition from solution. The rate of deposition will accordingly be increased and that of solution decreased; consequently the electrical charge will accumulate until the two processes occur at equal rates.

Butler § has shown that an adequate and physically acceptable basis for the Nernst formula is to hand when the conditions at the boundary surface of a reversible electrode are subjected to

* See Rideal, *Trans. Farad. Soc.*, **19**, 667 (1924).

† *Phys. Rev.*, **20**, 174 (1922).

‡ *Loc. cit.*

§ *Trans. Farad. Soc.*, **19**, 729 (1924).

statistical analysis. The considerations advanced are similar to those used by Langmuir in the theoretical treatment of the kinetics of vaporisation and heterogeneous gas reactions. An equation is obtained in which the electrode potential is represented as the sum of the heat absorbed in the passage of the metal ions into solution and a quantity which is determined by the statistical conditions at the surface of the electrode. His formula is,

$$\pi = \frac{E}{\nu F} + \frac{RT}{\nu F} \log k + \frac{RT}{\nu F} \log C, \quad (112)$$

in which E is the total energy change during the transfer of metal ions from the metal to the solution, and k is a small constant

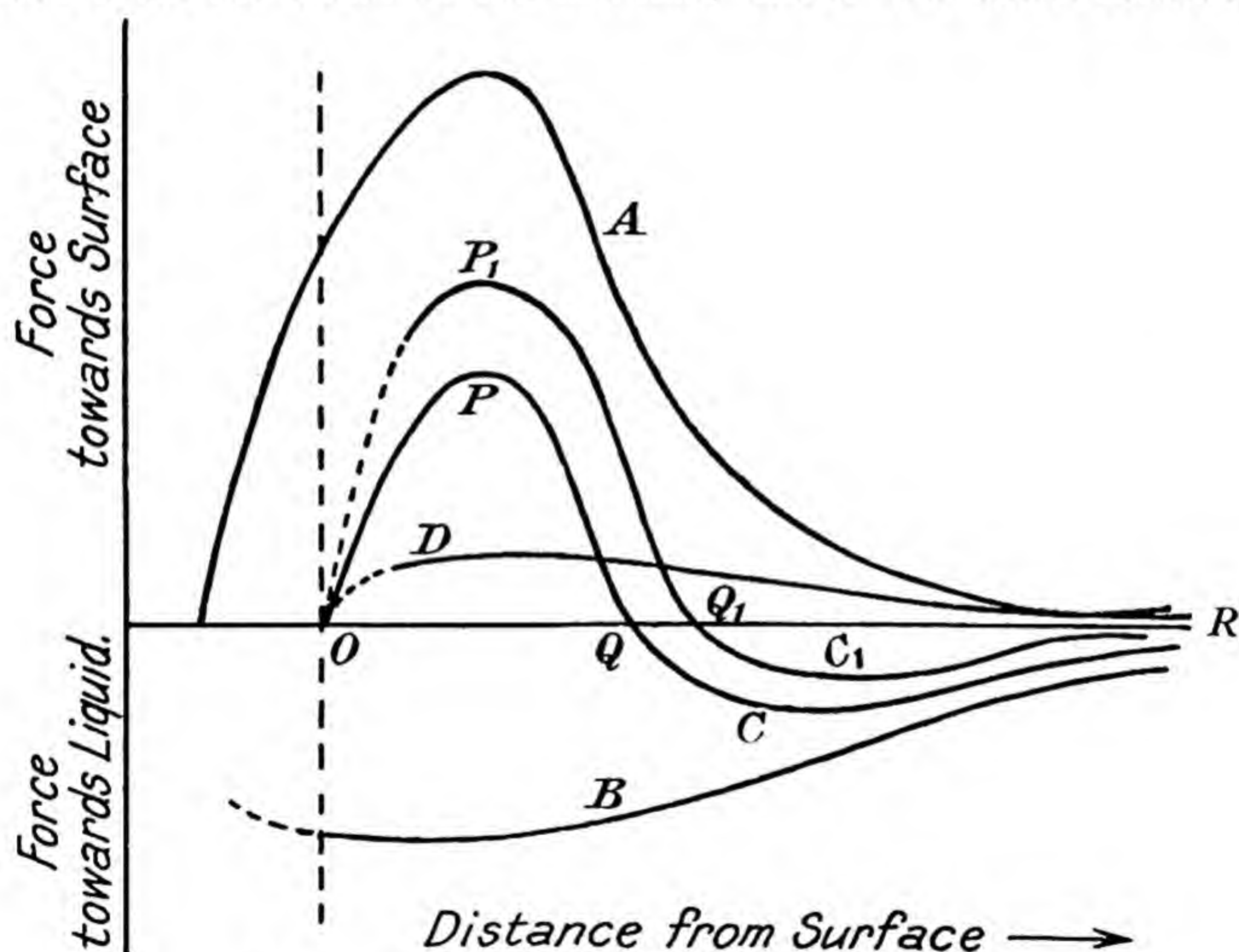


FIG. 21.—Butler's theory of electrode potential.

characteristic of the metal. The first two terms are equivalent to the Nernst solution pressure. Butler's hypothesis is as follows.

If we imagine that the ions are fixed in definite positions within a metal, the force of attraction is highly localised, *i.e.*, it falls off rapidly with distance as shown by the curve A (Fig. 21). Secondly, we have to take into account the attraction of the liquid upon the metal ions. This is greatest at the surface and falls off

on entering the liquid, curve B. The resultant of these opposing forces is given by curve C, with a balance point, in the general case, at Q.

Now consider how this disposition of forces will be modified by the existence of a potential difference at the surface. There is no reason for supposing that the positive ions, which have passed into solution, and the negative electrons, left in the metal, constitute a rigid electrical double layer. Undoubtedly the positive ions in solution will tend to arrange themselves as near as possible to the negatively charged surface, and therefore the electrical attraction on a positive ion will be greatest at the surface, gradually falling off as we penetrate into the zone of excess positive ions within the solution. This attraction is represented by curve D, and the result of the superposition of this term on the others is given by the curve C_1 with balance point Q_1 .

If the total potential difference between the surface of the metal and the interior of the solution is π , the work done by a positive gram-ion in passing from the surface into the interior of the solution is $\nu F\pi$, which is also equal to the area between the curve D and the two axes. In order that a gram-ion from the surface may reach the balance point, it must do an amount of work equal to the area P_1OQ_1 . This is composed of two parts, W_1' , the work done against the combined attractive process of the surface and the liquid in reaching Q_1 , and $-\nu\pi'F$, the work done against the electric field, π' being the potential difference between the surface and the balance point. Hence the total work done in reaching the balance point is $W_1' - \nu\pi'F$, and Butler gives the number of ions reaching it in unit time as

$$\theta_1 = N_1 A' \sqrt{T} e^{-\frac{W_1' - \nu\pi'F}{RT}},$$

where N_1 is the number of metal ions per sq. cm. in the surface layer of the metal, and A' is a constant.

Similarly, in reaching Q_1 from the interior of the liquid, a gram-ion does work represented by the area Q_1C_1R , where

$$Q_1C_1R = QCR - Q_1C_1RCQ = W_2' + \nu\pi''F,$$

π'' being the potential difference between Q_1 and the interior of the solution. The number of ions reaching the balance point from the solution is then

$$\theta_2 = N_s A \sqrt{T} e^{-\frac{W_2' + \nu\pi''F}{RT}},$$

where N_s is the number of ions per c.c., and A is a constant.

For equilibrium $\theta_1 = \theta_2$, so that

$$\frac{W_2' - W_1'}{RT} + \frac{\nu F(\pi' + \pi'')}{RT} = \log \frac{N_s A}{N_1 A'}.$$

Now $W_2' - W_1' = E$, the heat absorbed in the passage of one gram-ion of the metal into the solution, and $\pi' + \pi'' = \pi$, whence equation (112) follows at once.

In view of the fundamental difference of attitude towards the Nernst conception, it is of interest to note that the equations derived by Rideal and Butler, for the potential difference, are of the same type, viz., $\pi = \phi + \frac{RT}{\nu F} \log f(M)$. In the one case ϕ represents the electron affinity and $f(M)$ the atomic volume of the metal, whilst in the other ϕ is the heat of solution of the ions and $f(M)$ is a quantity which depends on the number of metal ions per square centimetre of the metal surface, and for which a simple kinetic interpretation is suggested.

Heyrovský* has also discussed the factors determining the Nernst potential, and by means of a thermodynamical argument has obtained a somewhat similar expression,

$$\pi = -\frac{RT}{F} \log p - \frac{H}{F} + \frac{RT}{F} \log C,$$

where H is the free energy of solvation of the electrode ions, and p , which includes quantities which depend on the metal alone, is regarded as a real solution pressure. However, it may be noted that the electrode potentials, calculated by means of this expression, differ from the observed, much more widely than those obtained by assuming that the electrical energy is simply equivalent to the total energy of the cell, and it is concluded, from a somewhat similar argument, that the metal contact potential difference is small—not greater than 0.2 volt—which is contrary to a large body of experimental evidence.

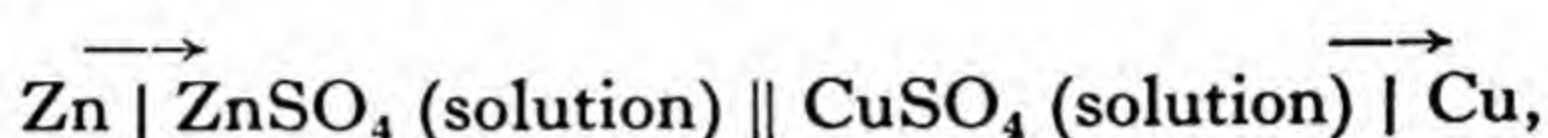
Heyrovský† also regarded the electrode as being continuously bombarded by hydroxyl ions, some of which react with the metallic atoms on the surface to form a metallic hydroxide, which passes into solution. The electrode is thus left with a negative charge, which increases in amount until it abstracts as many positive metallic ions, per second, as are removed by the hydroxyl ions. The objection to this theory is that no other ion except

* *Jour. Phys. Chem.*, **29**, 406 (1925).

† *Proc. Roy. Soc., A*, **102**, 628 (1922).

hydroxyl is considered as active. Furthermore, it is tacitly assumed that all metals acquire a negative charge when immersed in aqueous solution, and certain electro-capillary experiments, to be described later, show that this is not the case.

79. Variation of the electromotive force of a cell with concentration.—If we assume that a voltaic cell is composed of reversible galvanic elements, such as $M | MX$, $MX || M_1X_1$, $M_1X_1 | M_1$, it is evident that the electromotive force of the cell is equal to the algebraic sum of the potential differences that exist across the various junctions. Thus in a Daniell cell we have the scheme,



and there are four interfaces at which a potential difference exists. That at the $CuSO_4 \text{ (solution)} || ZnSO_4 \text{ (solution)}$ interface is very small, and the same remark applies to the potential difference at the $Zn | Cu$ junction (the Volta effect), so there remain the potential differences at the two metal-solution junctions. Thus, the electromotive force, E , of the cell is, from equation (110),

$$E = \frac{RT}{\nu F} \left[-\log \frac{P_1}{p_1} + \log \frac{P_2}{p_2} \right], \quad . \quad . \quad (113)$$

where p_1 and p_2 are the solution pressures of the zinc and copper ions, respectively, and P_1 and P_2 , the osmotic pressures of these ions in the respective solutions. As regards the signs used in this expression, it must be noted that when *positive* ions pass *from* the metal *to* the solution, the interfacial potential difference is written as *negative*, whereas it is denoted by the *positive* sign when the *positive* ions tend to pass *from* the electrolyte *to* the metal. The direction in which the positive ions tend to move is also that in which the positive current of electricity tends to pass through the cell, the movement of the ions with their associated charge constituting the current. For normal solutions of the two electrolytes at 18° C., the values of $\frac{RT}{\nu F} \log \frac{P_1}{p_1}$ and $\frac{RT}{\nu F} \log \frac{P_2}{p_2}$ are -0.522 volt and 0.581 volt, respectively, so that E is equal to 1.103 volts. Since equation (113) may be written in the form,

$$E = \frac{RT}{\nu F} \left[\log \frac{p_1}{p_2} + \log \frac{P_2}{P_1} \right], \quad . \quad . \quad (114)$$

or, at 18° C.,
$$\mathbf{E} = \frac{0.58}{\nu F} \left[\log_{10} \frac{p_1}{p_2} + \log_{10} \frac{P_2}{P_1} \right], \quad (115)$$

it is evident that the value of the electromotive force will increase as P_2 rises and P_1 decreases, *i.e.*, as the concentration of the copper sulphate solution is raised, and that of the zinc sulphate solution lowered. If $P_1 = p_1$ and $P_2 = p_2$, $\mathbf{E} = 0$, and there is neither deposition nor solution of ions at either electrode, the interfacial potential difference in each case being zero. As a rule the varia-

tion in the value of the term $\log_{10} \frac{P_2}{P_1}$ with change in concentration is small, since if P_2 or P_1 is changed a hundred-fold, ν being equal to two for the Daniell cell, the corresponding variation in the value of the term is only 0.058 volt.

The influence of concentration upon the value of the electromotive force of any cell may also be expressed in a slightly different manner thus :

Let π_1 be the potential difference at a metal-solution interface, the concentration of the solution being C_1 , so that the osmotic pressure can be written equal to kC_1 , where k is a constant. If ν_1 is the valency of the ions and p_1 the solution pressure, then from equation (111),

$$\pi_1 = \frac{0.058}{\nu_1} \log_{10} \frac{kC_1}{p_1},$$

and for another metal-liquid interface,

$$\pi_2 = \frac{0.058}{\nu_2} \log_{10} \frac{kC_2}{p_2}.$$

If the concentrations are changed to C_1' and C_2' , respectively,

$$\pi_1' = \pi_1 + \frac{0.058}{\nu_1} \log_{10} \frac{C_1'}{C_1},$$

and
$$\pi_2' = \pi_2 + \frac{0.058}{\nu_2} \log_{10} \frac{C_2'}{C_2},$$

so that the E.M.F., \mathbf{E}' , of the cell, formed with the two voltaic elements at the second concentrations, is given by

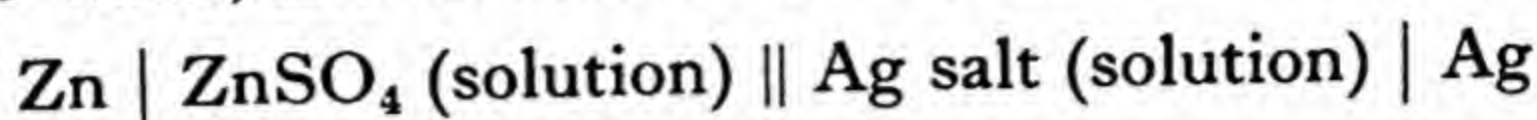
$$\mathbf{E}' = \pi_2' - \pi_1' = \pi_2 - \pi_1 + 0.058 \left[\frac{1}{\nu_2} \log_{10} \frac{C_2'}{C_2} - \frac{1}{\nu_1} \log_{10} \frac{C_1'}{C_1} \right],$$

the liquid-liquid junction potential difference being neglected,

i.e.,
$$\mathbf{E}' = \mathbf{E} + 0.058 \left[\frac{1}{\nu_2} \log \frac{C_2'}{C_2} - \frac{1}{\nu_1} \log \frac{C_1'}{C_1} \right].$$

E is the E.M.F. of the cell at the electrolytic concentrations C_1 and C_2 , the metals in both cases being assumed positive with respect to their solutions.

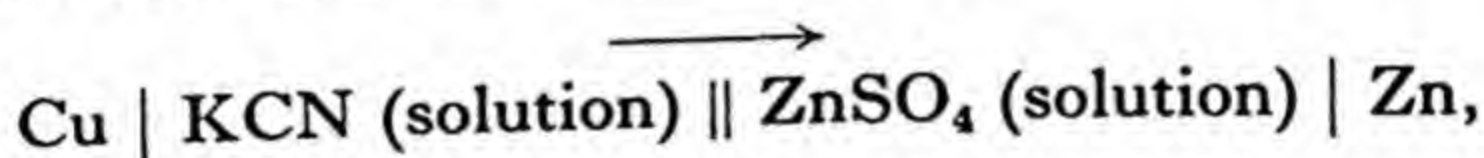
For sparingly soluble salts, such as silver halides, the osmotic pressure is small, and therefore the E.M.F. of a cell of the type



varies with the nature of the silver salt. If P is small, as it is for the chlorides, bromides and iodides, then from equation (113) we should expect the E.M.F. to be less than if the more soluble salts, such as silver nitrate, *etc.*, are used. This conclusion is verified as shown by the following results:—

silver salt	sulphate	nitrate	chloride	bromide	iodide
E.M.F. (volts)	1.54	1.53	1.10	0.91	0.71

Similarly, any process which lowers the solubility, such as adding other salts containing a common anion, will still further decrease the electromotive force. Potassium cyanide, added to the copper sulphate solution in a Daniell cell, first precipitates the copper and then redissolves it in excess, the solution no longer showing the blue coloration indicative of copper ions. Probably the double cyanide $\text{K}_2\text{Cu}(\text{Cn})_4$ is formed which is dissociated to a minute extent into Cu^{++} ions. Thus the concentration of the copper ions is lowered so much that the potential of the copper electrode is reduced below that of zinc, and the current in the cell,



does not pass in the expected direction, but from the copper to the zinc through the solution.

80 Standard electrodes.—The electromotive force of any cell is composed of at least two parts, namely, the potential differences existing at the two liquid-metal junctions, and in order to measure the potential difference at any solution-metal junction there must be incorporated with the junction another solution-metal interface of which the potential difference is known, or is zero. This *standard electrode*, or *half-cell* as it is sometimes called, must have a constant potential difference, it should be easily set up, and, to act as a standard, it must yield reproducible values of the potential difference under the same concentration and temperature conditions. In addition, it should possess as small a temperature coefficient as possible.

One such type of standard electrode is the *calomel half-cell*,

commonly called a *calomel electrode*, and shown in Fig. 22. A pool of pure mercury is covered with a layer of very pure calomel, Hg_2Cl_2 , and over all is a solution of potassium chloride, having a definite concentration, and saturated with calomel. One of three concentrations of potassium chloride is usually employed—either 0.1 normal, 1.0 normal or a saturated solution of potassium chloride—and half-cells with these concentrations are usually referred to as *tenth normal*, *normal* and *saturated calomel electrodes*, respectively. External connection is made by means of a platinum wire immersed in the mercury. Mercury ions are deposited from the solution upon the mercury electrode, which thus becomes positively charged.

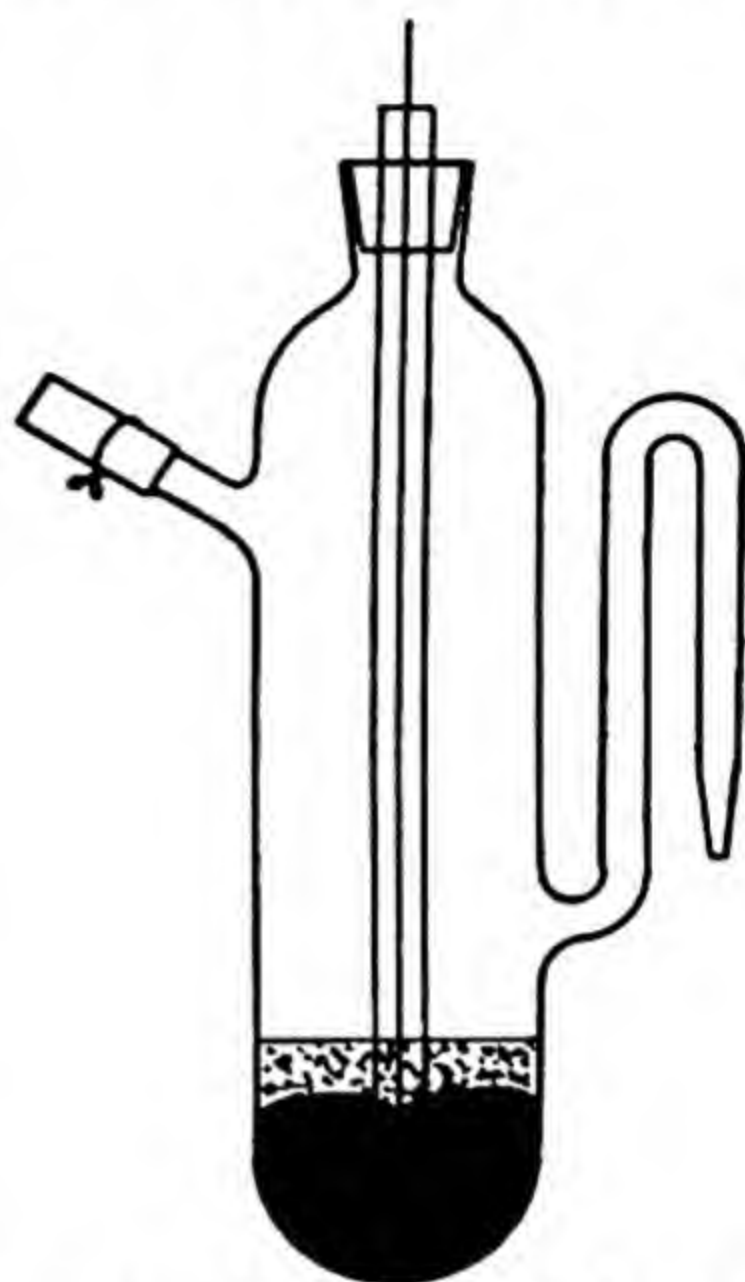
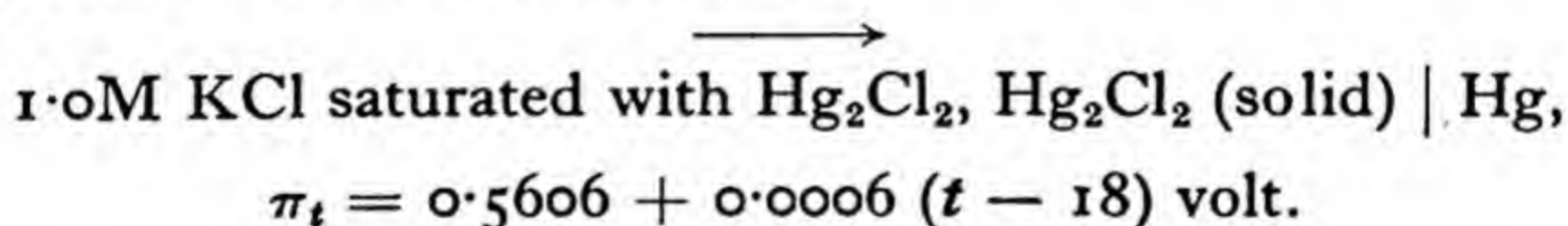


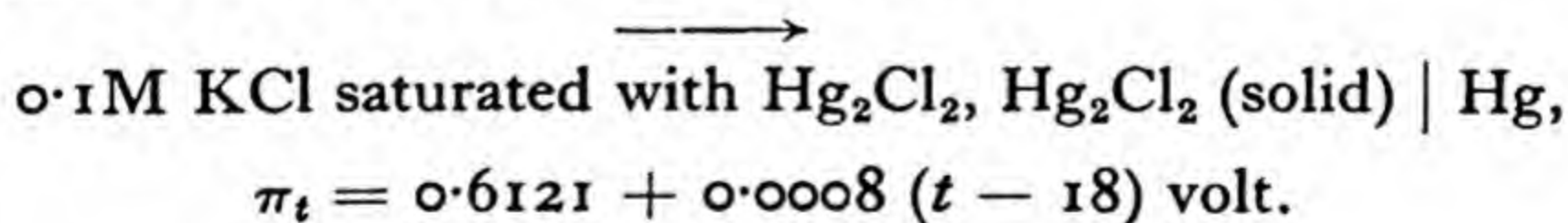
FIG. 22.—The calomel electrode

The values of the potential, π_t , of the electrode in these three half-cells, at a temperature $t^\circ \text{C}$. are given by means of the following formulæ:—*

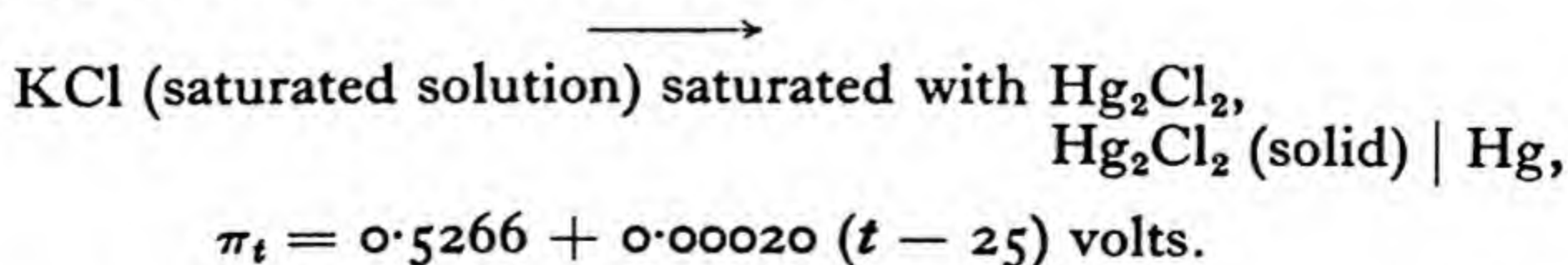
Normal calomel electrode :



Tenth normal calomel electrode :



Saturated calomel electrode :



* Fales and Vosburgh, *Jour. Amer. Chem. Soc.*, 40, 1291 (1918); Fales and Mudge, *ibid.*, 42, 2434 (1920).

Hydrochloric acid is sometimes substituted for the potassium chloride. Thus Fales and Mudge* quote the following values for the electrode potential of calomel half cells containing this acid, at 25° C.,

1.0M HCl saturated with Hg_2Cl_2 , $\text{Hg}_2\text{Cl}_2 \mid \text{Hg}$. . . 0.5567 volt.

0.1M HCl saturated with Hg_2Cl_2 , $\text{Hg}_2\text{Cl}_2 \mid \text{Hg}$. . . 0.6168 volt.

These values are based largely on Palmaer's value,† 0.560 volt, for the absolute potential of mercury in contact with 1.0 normal KCl, saturated with calomel, in the presence of solid calomel at 18° C. This result is not generally accepted, since it has been shown that the value does not represent the absolute potential of the mercury. For this reason it has been agreed that some one half-cell shall be made the standard of reference. The hypothetical *normal hydrogen electrode* has been agreed upon as a standard of reference, and potentials of calomel half-cells are now referred to that standard as having zero potential difference.

81. The normal hydrogen electrode.—So far we have considered the potential difference that exists at the junction of a metal and a solution of its salt. This effect is not confined to metals, but various gases are found to act in a similar manner, when means are devised to bring them into a form, as easily handled as are metal electrodes. Hydrogen is the most important of these gases, and the way in which it can be utilised to act as an electromotively active gas, is to absorb it in a metal such as platinum, palladium, or iridium which, in a finely divided condition holds large quantities of hydrogen. A metal, thus loaded with hydrogen, forms what is termed a *hydrogen electrode*. It can be brought into equilibrium with hydrogen ions in a solution in the same manner as mercury is brought into equilibrium with mercury ions; the higher the concentration of the hydrogen ions in the surrounding solution, the more positive becomes the hydrogen electrode. Provided that the hydrogen gas pressure around the electrode, and the concentration of the hydrogen ions within the solution, both remain constant, we have, between the electrode and the solution, a potential difference which remains constant, as long as the physical conditions remain constant. In addition, it is easily reproduced. The electrode will, therefore, form a standard of potential against which the potential difference at any other metal-solution interface can be measured, provided that the latter can be suitably combined with the hydrogen electrode.

* *Loc. cit.*

† *Zeits. phys. Chem.*, 59, 129 (1907).

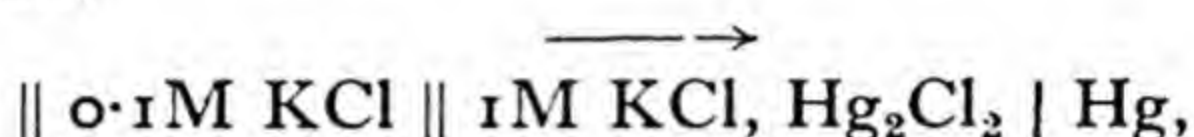
We may define the potential of the latter as zero at all temperatures, other electrode potentials being expressed in terms of the hydrogen electrode potential as zero. In practice, the hydrogen is under one atmosphere pressure, and the electrode—platinised platinum—dips in a normal solution of hydrogen ions, *i.e.*, one containing 1.008 grams of hydrogen ions per litre of solution.

Assuming that 0.560 volt is the absolute potential of mercury in contact with 1.0 normal KCl, saturated with calomel, in the presence of solid calomel at 18° C., Fales and Vosburgh quote the following values for the hydrogen electrode potential:—

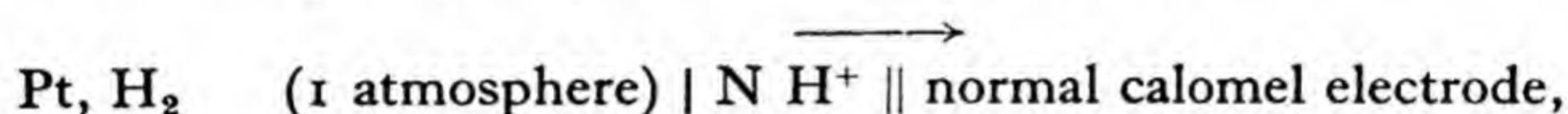
$$\parallel 1.0M \text{ HCl} \mid \text{H}_2 (1 \text{ atmosphere}), \text{Pt} \cdot 0.2777 \text{ volt.}$$

$$\parallel 0.1M \text{ HCl} \mid \text{H}_2 (1 \text{ atmosphere}), \text{Pt} \cdot 0.2179 \text{ volt.}$$

Lewis and Randall,* defining the normal calomel electrode as the combination,



determined, at 25° C., the E.M.F. of the cell,



to be 0.2822 volt. If we take the absolute potential of the normal calomel electrode to be 0.5648 volt at 25° C., the absolute potential of the normal hydrogen electrode is + 0.2826 volt.

The influence of the partial pressure of the hydrogen gas on the hydrogen-electrode potential has been investigated by Loomis and Acree. The results show that in the neighbourhood of atmospheric pressure, the influence of the partial gas pressure on the potential of the hydrogen electrode can be expressed by means of the formula,†

$$E = \frac{RT}{2F} \log \frac{p_1}{p_2},$$

where p_2 and p_1 are the partial pressures of the gas. The average change in potential was found to be 0.00001751 volt per mm. of mercury pressure change, and this value agreed closely with that calculated by means of the above formula, namely 0.00001746 volt.

To prepare the hydrogen electrode, a preliminary plating of gold on platinum foil is recommended by Lewis, Brighton and Sebastian,‡ since gold, unlike platinum, does not absorb large

* *Jour. Amer. Chem. Soc.*, **38**, 2391 (1916).

‡ *Jour. Amer. Chem. Soc.*, **39**, 2245 (1917).

† See section 100.

amounts of gases, and therefore comes to the equilibrium state more quickly. For the actual plating of the platinised-platinum electrode, Popoff, Kunz and Snow* recommend that, if it is an old one, it should be cleaned by electrolysis of a concentrated solution of hydrochloric acid, using the electrode as the anode. If it is a new one, it may be cleaned in hot alkali. After the cleaning process, it is made the kathode during the electrolysis of a dilute potassium cyanide solution of gold, and then, still acting as the kathode, a 3 per cent. solution of chloroplatinic acid, containing 0.5 c.c. of 0.1N lead acetate in 100 c.c., is electrolysed for five minutes. With the electrode as kathode, a dilute solution of sodium hydroxide is electrolysed for a few seconds, and afterwards follows electrolysis in dilute sulphuric acid for one minute. Finally, the electrode is washed with distilled water. Other workers, however, prefer their own method of preparation. In use the hydrogen electrode is immersed in an acid solution, hydrogen gas being bubbled through the solution and around the platinum, until the measured electromotive force of the cell, of which the electrode forms part, is constant. Usually, after the gas has bubbled through for about thirty minutes, equilibrium is attained. There are many forms of hydrogen half-cell, but that shown in Fig. 23 is extensively used. Hydrogen gas enters by the inlet A, and bubbles past the electrode B. In this manner the gas can be maintained at atmospheric pressure. It is found that the shape and size of the cell determine the time taken to reach equilibrium. The speed of attainment of this condition is also determined by the traces of impurities, such as oxygen, which may be present.

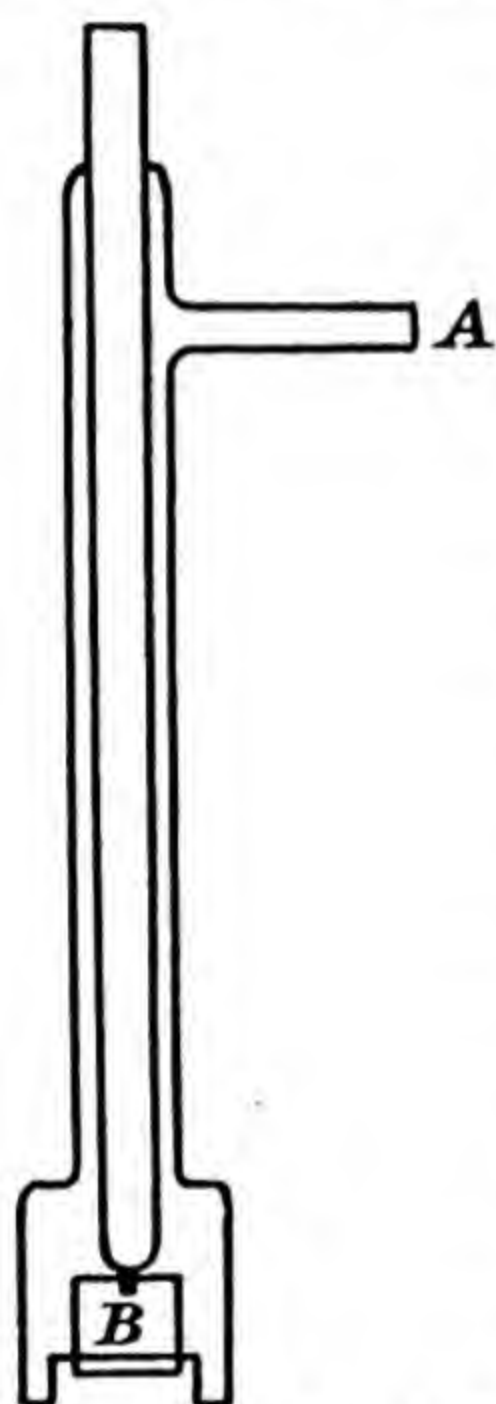


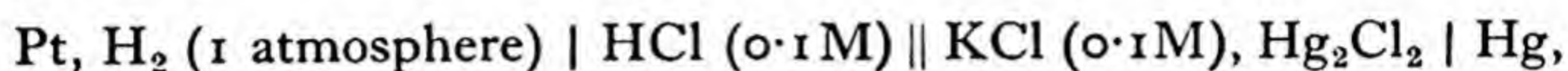
FIG. 23.—A hydrogen electrode.

Two hydrogen half-cells may be combined to form a hydrogen concentration cell by allowing siphon tubes to pass, from each half-cell, into an intermediate vessel which contains a normal acid solution, the gas pressure in the two half-cells being different.

82. Working standard half-cells.—It is more convenient to substitute for the hydrogen half-cell a *working standard*,

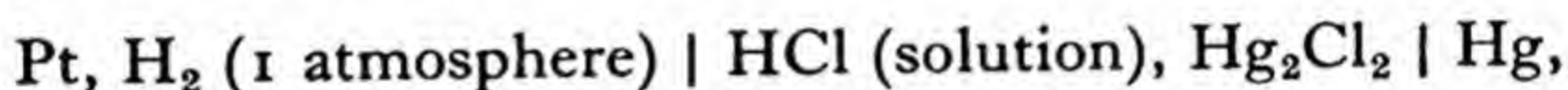
* *Jour. Phys. Chem.*, 32, 1056 (1928).

such as the calomel half-cell. The latter may be joined, by means of a suitable bridge, to the standard hydrogen half-cell, and the electromotive force of the combination measured. By combining the working standard half-cell with any other half-cell, the potential difference at any metal-solution junction can be determined with reference to the working standard, and finally referred to the standard hydrogen electrode as the zero of potential. The system,



has been carefully studied by several workers. The results which have been obtained at 25°C. , after correction for the vapour pressure of the solution, give a mean of 0.4272 volt.^* This value includes the contact potential existing between 0.1 molal HCl and 0.1 molal KCl . Lewis \dagger calculated that this potential amounts to 0.0284 volt . Bjerrum \ddagger obtained the value 0.0278 volt .

The electromotive force of this type of cell varies with the temperature. Ellis \S measured the E.M.F. of the cells,



at 18°C. , 25°C. and 35°C. , the concentration of the acid varying from 0.033 to 4.5 molal . His results are given in Table LI. :—

TABLE LI.

E.M.F. OF HYDROGEN—CALOMEL CELLS AT DIFFERENT TEMPERATURES.

Moles of HCl in 1000 Gms. of Water.	E.M.F. (Volt) at		
	18°C.	25°C.	35°C.
4.484	0.15759	0.15506	0.15124
1.9278	0.23769	0.23589	0.23304
1.0381	0.27919	0.27802	0.27595
0.77137	0.29654	0.29571	0.29411
0.50948	0.31912	0.31865	0.31765
0.33757	0.33845	0.33836	0.33794
0.10040	0.39764	0.39884	0.40013
0.03332	0.45020	0.45258	0.45557
0.01001	0.5271	0.5302	0.5369

* See Loomis and Meacham, *Jour. Amer. Chem. Soc.*, **38**, 2310 (1916).

\dagger *Ibid.*, **36**, 1973 (1914).

\ddagger *Zeits. Elektrochem.*, **17**, 61 (1911).

\S *Jour. Amer. Chem. Soc.*, **38**, 737 (1916).

The various working standard electrodes, which are in general use, include the following :—

	E.M.F. (volt) at		
	0° C.	18° C.	25° C.
KCl (0.1N), Hg ₂ Cl ₂ Hg	0.337	0.337	0.337
KCl (1.0N), Hg ₂ Cl ₂ Hg	0.289	0.286	0.285
Hg ₂ SO ₄ (0.1N—0.5N), Hg ₂ SO ₄ Hg	—	0.68	—
KOH (1.0N), HgO Hg	0.130	—	0.107
NaOH (1.0N), HgO Hg	0.133	—	0.111
NaOH (0.1N), HgO Hg	0.184	—	0.166

Instead of these mercury electrodes another half-cell, Ag | AgCl, chloride solution, commonly called the *silver-silver chloride electrode*, is in common use. Silver is deposited electrolytically upon platinum foil, and is then covered with an electrolytic deposit of silver chloride. Scatchard * gives 0.0453 volt at 25° C. for the potential of the cell,

Hg | Hg₂Cl₂, KCl (saturated) || KCl (0.1M), AgCl | Ag,
and 0.0466 volt at 25° C. for the potential of the cell,

Ag | AgCl, KCl (0.1M) || KCl (0.1M), Hg₂Cl₂ | Hg.

The silver-silver chloride electrode has been used recently by Buckley and Hartley † in their work with methyl alcohol as the solvent in concentration cells. They found it to be very suitable as a reference standard, provided that it was freshly prepared.

Another interesting electrode is that known as the *glass electrode*. If we have an arrangement such as this,

Hg | Hg₂Cl₂, KCl (sat.) || sol. A | sol. B || KCl (sat.), Hg₂Cl₂ | Hg
a *b* *c* *b'* *a'*

the potential differences at *a* and *a'* are equal, and opposite, and if we suppose that the liquid-junction potentials at *b* and *b'* balance, there only remains that at the junction *c*. We can imagine that there is at *c* some material which permits the passage of a particular kind of ion between the solutions A and B, this ion passing from the place of higher to that of lower concentration. Representing this ion by the symbol X, the electromotive force of the whole cell is given by

$$E = \frac{RT}{\nu F} \log \frac{[X_B]}{[X_A]}.$$

Haber and Klemeniewicz ‡ found that, if a very thin glass partition were placed at *c*, the resultant E.M.F. of the cell agreed with that calculated from the above formula. The latter, however,

* *Jour. Amer. Chem. Soc.*, 47, 696 (1925).

† *Phil. Mag.*, 8, 320 (1929).

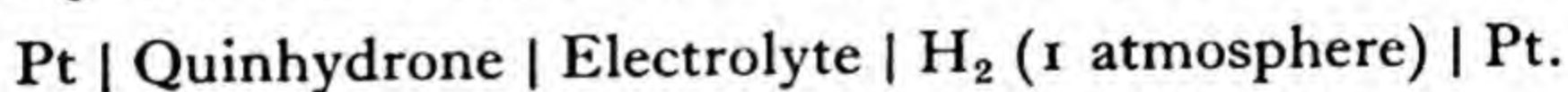
‡ *Zeits. phys. Chem.*, 67, 385 (1909).

expresses the experimental results only under particular conditions; the kind of ions in solution, and the nature of the glass, both affect the results. The cell is used to measure the hydrogen ion concentration in different solutions.

83. The quinhydrone electrode.—Bülmann* has shown that the usual hydrogen electrode may, in several cases, be replaced by a quinhydrone electrode, formed by dissolving a small quantity of quinhydrone in the electrolyte under investigation, and placing a piece of bright platinum in the solution. The quinhydrone then represents a potential pressure of hydrogen which is constant, but very feeble. The quinhydrone electrode functions as a hydrogen electrode, with a hydrogen gas pressure of $10^{-24.40}$ atmospheres at 18°C. , and $10^{-23.34}$ atmospheres at 25°C. Against a hydrogen electrode, with a pressure of hydrogen equal to one atmosphere, it has a potential of 0.7044 volt at 18°C. , the electrolyte being 0.1N hydrochloric acid; in other dilute acids very nearly the same potential is reached.

Bülmann and Lund† have shown, further, that in more concentrated solutions the simple quinhydrone electrode may be replaced by an electrode which contains quinhydrone and an excess of either quinol or quinone. These electrodes are named hydro-quinhydrone and quino-quinhydrone electrodes, respectively.

The quinhydrone electrode is so simply prepared, acquires its potential so rapidly, and preserves its constancy for so long, that it may usefully replace the hydrogen, or calomel electrode. Measuring the electromotive forces of cells such as



Bülmann and Krarup‡ found that the relationship between the potential and the temperature was linear, and on plotting the results, the potential of the quinhydrone electrode, π_t , at a temperature $t^{\circ}\text{C.}$ was given by

$$\pi_t = .7175 - 0.00074 t.$$

It has been used in methyl alcohol by Ebert,§ who measured the hydrogen and quinhydrone electrodes, successively, in portions of the same solution against an aqueous calomel reference standard. For the potentials of these electrodes, he obtained concordant values, 0.724 volt, at 18°C. Buckley and Hartley||

* *Ann. Chim.*, 15, 109 (1921).

† *Jour. Chem. Soc.*, 125, 1954 (1924).

‡ *Phil. Mag.*, 8, 320 (1929).

§ *Ibid.*, 16, 327 (1921).

|| *Berichte*, 58, 175 (1925).

could not get steady values with methyl alcohol, the approximate values being 0.716-0.719 volt. The E.M.F. of the cell varied with stirring, with the addition of further quantities of quinhydrone to the solution, and with heating the platinum electrode to redness.

There are many forms of electrode vessels, but that shown in Fig. 24 is found to be very convenient for quinhydrone electrodes.

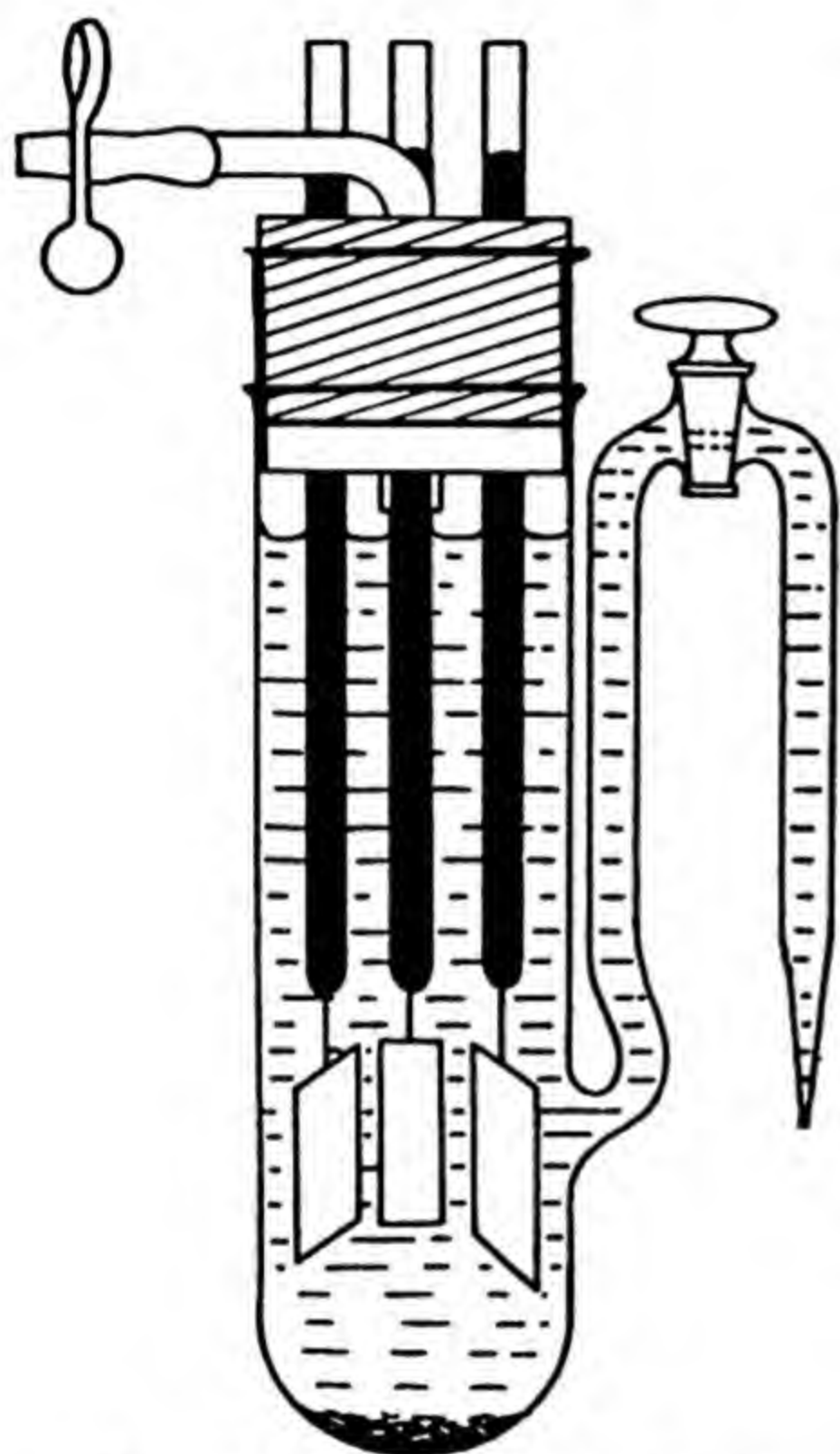


FIG. 24.—The quinhydrone electrode.

The vessel contains three electrodes, isolated from one another. Measurements should be made with more than one electrode, as it is found in practice that the electrode is greatly affected by the presence of small quantities of impurities.

84. Dropping electrodes.

—Consider a vessel A (Fig. 25), containing an electrolytic solution into which dips a fine jet, B, the latter connected to a mercury reservoir. A fine jet of mercury, falling from B, collects on a pool of mercury at C, covered with a mercurous salt which prevents polarisation* at this interface. If the osmotic pressure of the mercury ions in the solution is greater than the so-called solution pressure of the mercury, there will be a deposition of positive charge on the drop falling from the jet. Just before the drop breaks away it has received a deposition of

positive ions upon it, and when the drop falls, they are carried away with it. Hence the new mercury surface exposed in the jet is uncharged. This charging up of the surface takes place comparatively slowly, so that if the drops follow one another very quickly there will be no time for the mercury ions to pass from the solution on to the mercury drop before the latter breaks away. For this reason Helmholtz† assumed that the dropping electrode had no surface charge; in other words, there is no potential difference between the mercury in the jet B and the solution immediately in contact with it. Thus with this arrangement

* See Chapter VIII.

† *Zeits. phys. Chem.*, 4, 150 (1889).

the measured potential difference between the mercury electrodes C and B was taken as equal to that existing between the pool of mercury C and the surrounding electrolyte.

Palmaer * pointed out that if the mercury ions did collect on the drop and were carried away with it, the concentration of the solution near the orifice of the jet would alter, and therefore the null potential difference between the jet and the solution would only occur if the osmotic and solution pressures were

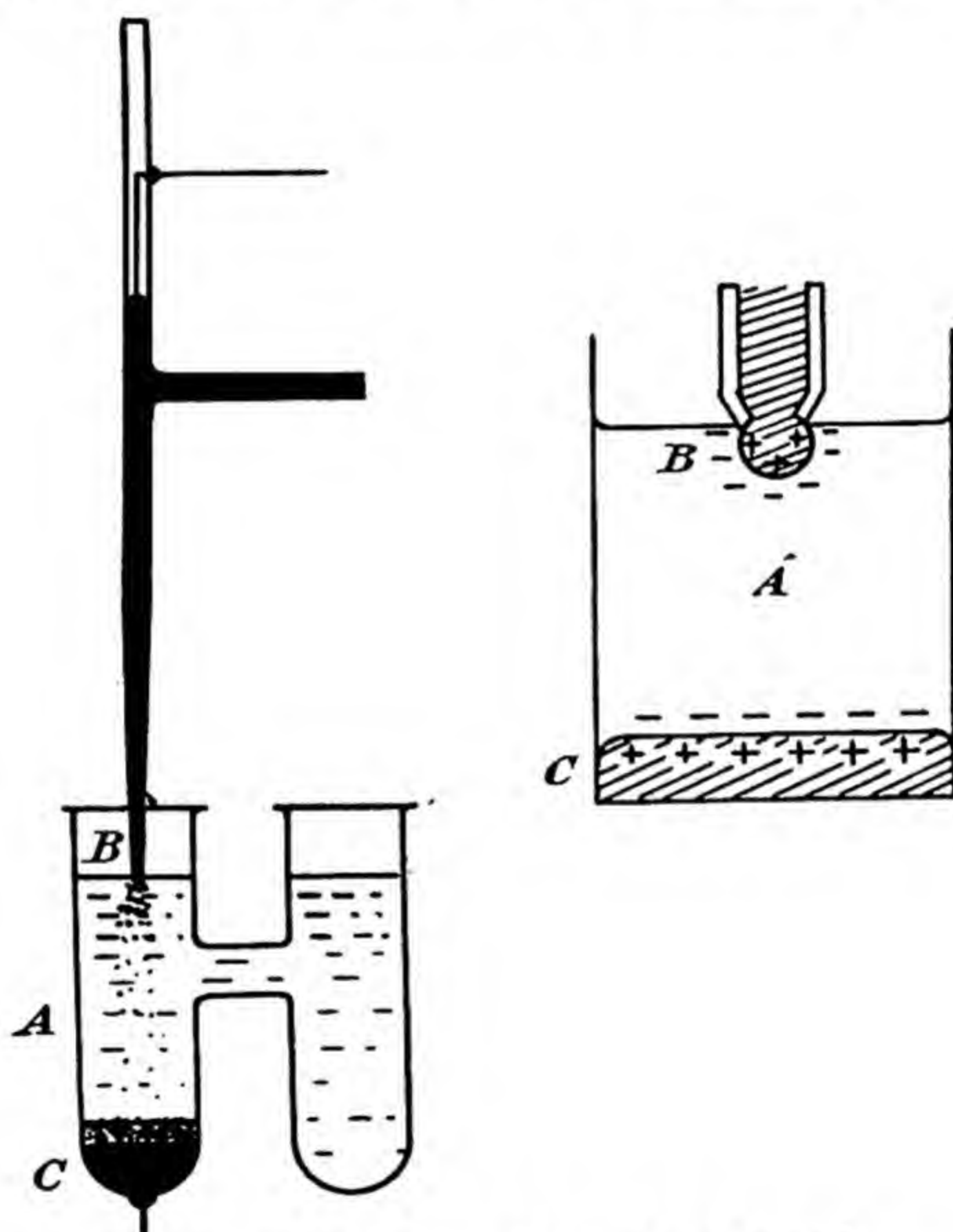


FIG. 25.—The mercury dropping electrode.

equal. These conditions are not easily obtained, but if the solution is, approximately, of the correct concentration, the falling mercury does, in time, bring about the appropriate conditions within the vicinity of the jet. The actual concentration of the mercury ions required was found to be very small. He used solutions of potassium chloride and potassium cyanide, each containing mercuric cyanide. The dropping electrode formed one

* *Zeits. phys. Chem.*, 25, 265 (1898); 28, 257 (1899); 36, 664 (1901).

half of a cell and a calomel electrode the other half, the electromotive force of the cell, thus formed, being measured at different times. Assuming the potential of the dropping electrode to be zero, his final result for the potential of the normal calomel electrode was 0.5732 ± 0.0003 volt at 18°C. , a correction being applied for any liquid-liquid junction potential difference. He also found that by adding certain substances to a 0.1N KCl solution, he could reduce the observed potential difference between the still and dropping mercury until it became zero.

Smith and Moss,* however, pointed out that Palmaer's conclusions were of doubtful validity. They examined several so-called null-solutions, for which the potential difference between the still and mercury dropping electrodes, in contact with the solution, is zero, and found that the potential differences between different null-solutions and mercury are not the same. In their experiments they measured each potential difference against the potential difference of the junction $\text{Hg} | \text{KCl} (0.1\text{N})$, and also one null-solution against another. Their results showed that if the null-solution potential differences are assumed to be zero, then the values obtained for the potential difference $\text{Hg} | \text{KCl} (0.1\text{N})$ vary from about 0.53 to 0.79 volt. Accordingly, they concluded that the potential difference between mercury and these null-solutions is not necessarily zero.

Smith † had previously measured the electromotive forces of cells $\text{Hg} | \text{KI} || \text{KCl} \downarrow$, in which the vertical arrow signifies the dropping electrode, and obtained the following results :—

$$\downarrow \text{KCl}(0.5\text{N}) || \text{KCl}(0.5\text{N}) | \text{Hg}_2\text{Cl}_2 | \text{Hg} = 0.522 \text{ volt.}$$

$$\downarrow \text{KI}(0.5\text{N}) || \text{KCl}(0.5\text{N}), \text{Hg}_2\text{Cl}_2 | \text{Hg} = 0.784 \text{ volt.}$$

$$\downarrow \text{KI}(0.5\text{N}) || \text{KI}(0.5\text{N}), \text{Hg}_2\text{I}_2 | \text{Hg} = 0.383 \text{ volt.}$$

$$\downarrow \text{KCl}(0.5\text{N}) || \text{KI}(0.5\text{N}), \text{Hg}_2\text{I}_2 | \text{Hg} = 0.127 \text{ volt.}$$

The first and second of these values give 0.262 volt, and the third and fourth, 0.256 volt, as the potentials of the liquid junction, $\text{KI}(0.5\text{N}) || \text{KCl}(0.5\text{N})$, whereas we know that this potential is extremely small.

Nernst ‡ worked out the theory of the dropping electrode in accordance with his idea of electrolytic solution pressure. The fresh surface of the mercury jet charges itself as it enters the solution, and hence removes mercurous ions from the solution or gives them off to it. The solution must, therefore, continue to become richer or poorer in mercurous ions at the point of entry

* *Phil. Mag.*, 15, 478 (1908).

† *Phil. Trans.*, A, 193, 47 (1900).

‡ *Loc. cit.*

of the jet until no further tendency to exchange is present, until, therefore, the osmotic pressure and the solution pressure of the mercury opposed to it balance each other.

This view is only correct when the solution at the point of entry of the jet does not continually receive fresh mercurous ions by diffusion or convection, which would cause depolarisation of the mercury. Hence it is of advantage if the mercury jet itself only comes into contact with the solution over a very small space and time interval. It follows from this theory that mercury salt must be carried over from the dropping to the stationary electrode. Every fresh drop entering the solution charges itself, that is, mercurous ions are, as a rule, deposited upon it; and since a separation of anion and kation cannot occur, every drop is enveloped by a layer of anions. Below, where the mercury drops flow together, the salt carried down goes into solution. At the jet surface the concentration decreases, while below it increases. We should have, therefore, on account of the action of the interface potential difference, an *electrical adsorption* of the mercurous salt at the mercury surface. It would be distinguished from ordinary adsorption by the fact that it is determined by the concentration of the mercurous ions, and that it is negative for very small concentrations of mercurous ions.

85. Normal electrode potentials.—An accurate knowledge of the electrode potential, assumed by a metal in the presence of its ions within the surrounding solution, is important, since in many reactions the direction and value of this potential, relative to the electrolyte, determines the reaction. In practice, the metal-solution interface, the potential difference of which is required, is combined with a standard electrode to form a cell, and the electromotive force of the latter determined. The value thus obtained is the potential difference of the metal-solution interface, plus any liquid-liquid junction potentials occurring in the cell. If we neglect, eliminate, or calculate the latter, we obtain the potential of the electrode relative to that of the standard electrode.

Assuming that the absolute potential of the normal hydrogen electrode, relative to the normal hydrogen ion solution in contact with it, is $+0.2826$ volt, the absolute potential, π , of any electrode, and its potential referred to the normal hydrogen electrode, π_H , both at 25°C. , are related as follows,

$$\pi = \pi_H + 0.2826,$$

and referred to the normal calomel electrode, π_0 , at 25°C. ,

$$\pi = \pi_0 + 0.5648.$$

In equation (110) we may put P equal to $k[C]$, where k is a constant for any one metal, and $[C]$ the concentration of the metallic ions in the solution which surrounds the metal. Hence,

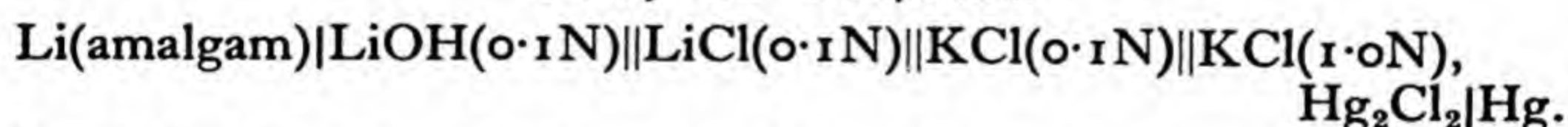
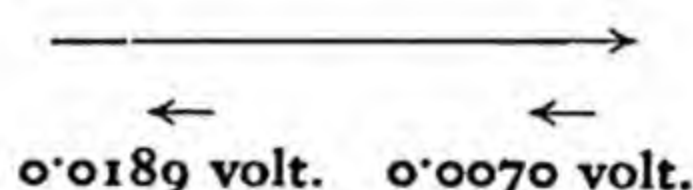
$$\pi = \frac{RT}{\nu F} \log \frac{k[C]}{p},$$

or

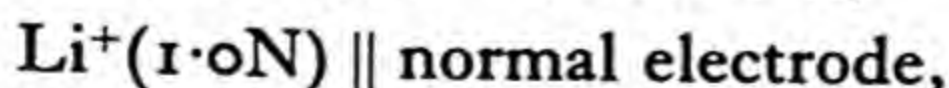
$$\pi = \pi_0 + \frac{RT}{\nu F} \log [C],$$

where π_0 , equal to $\frac{RT}{\nu F} \log \frac{k}{p}$, is the value of π when $[C]$ is unity, *i.e.*, when the concentration of the ions is normal. This constant, π_0 , is called the *normal electrode potential* and is an important characteristic of an element. Its value, referred to the normal hydrogen or calomel electrodes as zero, may be calculated from experimentally determined values of π .

As an example, consider the case of the lithium electrode whose potential has been determined, at 25° C., by Lewis and Keyes.* A cell containing one electrode of metallic lithium and the other of lithium amalgam, and an electrolyte of propyl amine saturated with lithium iodide was used, lithium iodide being soluble, and lithium insoluble in this solvent. The electromotive force of the cell was 0.9502 volt. They then measured the electrode potential of the amalgam in aqueous solution, using the following type of cell:—



Its E.M.F. was 2.3952 volts, but this includes several liquid potentials of which the one between 0.1 normal KCl and 1.0 normal KCl was neglected. These liquid potentials are inserted over the cell, and both oppose the main E.M.F. of the cell, and, therefore, the E.M.F., exclusive of liquid potentials, was $2.3952 + 0.0259 = 2.4211$ volts. If now we take the corrected degree of dissociation of 0.1N LiOH as 0.74, we may calculate the E.M.F. of a similar cell containing lithium ions at normal concentration. Thus the E.M.F. of the cell,



is $2.4211 - 0.0669 = 2.3542$ volts, and therefore the normal electrode potential of lithium amalgam against the calomel electrode

* *Jour. Amer. Chem. Soc.*, 35, 340 (1913).

is -2.3542 volts. To find the normal electrode potential of solid lithium, we need only to add the difference between the potentials of lithium and lithium amalgams given above, -0.9502 volt, and thus the normal potential of the lithium electrode is

TABLE LII.

NORMAL ELECTRODE POTENTIALS AT 25° C.

Electrode.	Potential in Aqueous Solutions, referred to		Potential in Methyl Alcohol Solutions, referred to	
	π_C (volts). Calomel Scale.	π_H (volts). Hydrogen Scale.	π_C (volts). Calomel Scale.	π_H (volts). Hydrogen Scale.
1. Li, Li^+	-3.2400	-2.9578		
2. Rb, Rb^+	-3.2064	-2.9242		
3. K, K^+	-3.2046	-2.9224		
4. Na, Na^+	-2.9948	-2.7126	-3.010	-2.728
5. Mg, Mg^{++} at 18° C.	-2.148	-1.866		
6. Zn, Zn^{++}	-1.0403	-0.7581		
7. Fe, Fe^{++}	-0.723	-0.441		
8. Cd, Cd^{++}	-0.6814	-0.3976	-0.540	-0.258
9. Tl, Tl^+	-0.6158	-0.3336	-0.661	-0.379
10. Ni, Ni^{++}	-0.527	-0.245		
11. Sn, Sn^{++}	-0.428	-0.136		
12. Pb, Pb^{++}	-0.414	-0.122		
13. Pt. H_2 , H^+	-0.2822	0	-0.2822	0
14. Cu, Cu^{++}	$+0.0647$	$+0.3448$	$+0.208$	$+0.490$
15. Hg, Hg_2^{++}	$+0.5106$	$+0.7986$		
16. Ag, Ag^+	$+0.5065$	$+0.7995$	$+0.482$	$+0.764$
17. Pt. O_2 , OH^-	$+0.1154$	$+0.3976$		
18. Pt. I_2 , I^-	$+0.3560$	$+0.5382$	$+0.087$	$+0.369$
19. Pt. Br_2 , Br^-	$+0.7837$	$+1.0659$	$+0.567$	$+0.849$
20. Pt. Cl_2 , Cl^-	$+1.0772$	$+1.3594$	$+0.846$	$+1.128$

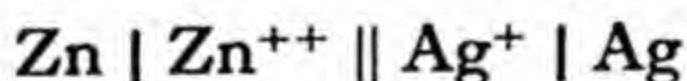
1. Lewis and Keyes, *Jour. Amer. Chem. Soc.*, **35**, 340 (1913).
2. Lewis and Argo, *ibid.*, **37**, 1983 (1915).
3. Lewis and Keyes, *ibid.*, **34**, 119 (1912).
4. Lewis and Kraus, *ibid.*, **32**, 1459 (1910).
5. Beck, *Rec. trav. chim.*, **41**, 353 (1922).
6. Horsch, *Jour. Amer. Chem. Soc.*, **41**, 1787 (1919).
7. Richards and Behr, *Zeits. phys. Chem.*, **58**, 301 (1907).
8. Horsch, *loc. cit.*
9. Gerke, see Lewis and Randall, *Thermodynamics*.
10. Haring and Bosch, *Jour. Phys. Chem.*, **33**, 161 (1929).
11. Noyes and Toabe, *Jour. Amer. Chem. Soc.*, **39**, 1537 (1917).
12. Gerke, *loc. cit.*
13. Beattie, *ibid.*, **42**, 1128 (1920).
14. Lewis and Lacey, *ibid.*, **36**, 804 (1914).
15. Linhart, *ibid.*, **38**, 2356 (1916).
16. Noyes and Brann, *ibid.*, **34**, 1016 (1912), and Kolthoff, *Z. anorg. Chem.*, **119**, 202 (1921).
17. Lewis and Randall, *loc. cit.*
18. McKeown, *Trans. Farad. Soc.*, **17**, 517 (1922).
19. Lewis and Storch, *Jour. Amer. Chem. Soc.*, **39**, 2544 (1917).
20. Lewis and Rupert, *ibid.*, **33**, 299 (1911).

— 3.3044 volts, referred to the calomel electrode as zero, or
 — 3.3044 + 0.2822 = — 3.0222 volts, referred to the normal hydrogen electrode as zero.*

The normal electrode potentials at 25° C. of various electrodes, referred both to the normal calomel electrode, π_C , as zero, and to the standard hydrogen electrode, π_H , as zero, are given in Table LII., a positive sign indicating that the metal is the positive electrode in a cell formed by combining the electrode with the standard electrode. Buckley and Hartley have recently determined the normal electrode potentials at 25° C. of a few electrodes in methyl alcohol as the solvent, and these are included in the table. All values refer to unit activity of the ions.

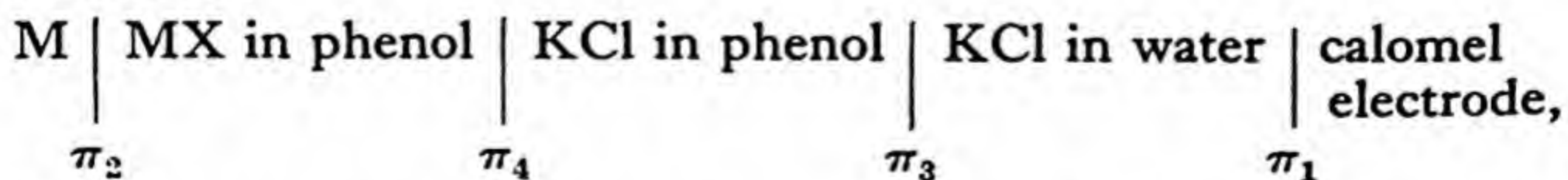
The normal electrode potentials, and the potentials of various half-cells, both on the hydrogen and normal calomel scales are shown in Fig 26. In addition, the supposed absolute potentials of these electrodes are indicated in the diagram.

The sequence in which the elements are arranged in Table LII. is that of the electromotive series and all metals with an electrode potential less than that of hydrogen displace hydrogen ions from solution. The electromotive force of a cell formed by combining any two normal electrodes is equal to the algebraic sum of their electrode potentials, due attention being paid to the direction of potential increase within the cell. Thus the electromotive force of the cell



is equal to $0.7887 - (-0.7581) = 1.5468$ volts.

A knowledge of one single potential difference is sufficient for the evaluation of all other potentials, as long as the solvent remains the same. When we pass from an aqueous solution to a non-aqueous one, we have to consider the potential difference at the boundary between the two solutions. Thus, consider a cell such as



where M represents the metal, and MX its salt. Of the various potentials, π_1 is known, π_3 is zero when the solutions are in equilibrium, and π_4 is a diffusion potential. Frequently π_4 may be

* If we define the normal electrode potential as being that value of the electrode potential when the activity of the ions is unity, the potential of the lithium electrode is — 2.9578 volts, referred to the normal hydrogen electrode as zero (see section 151).

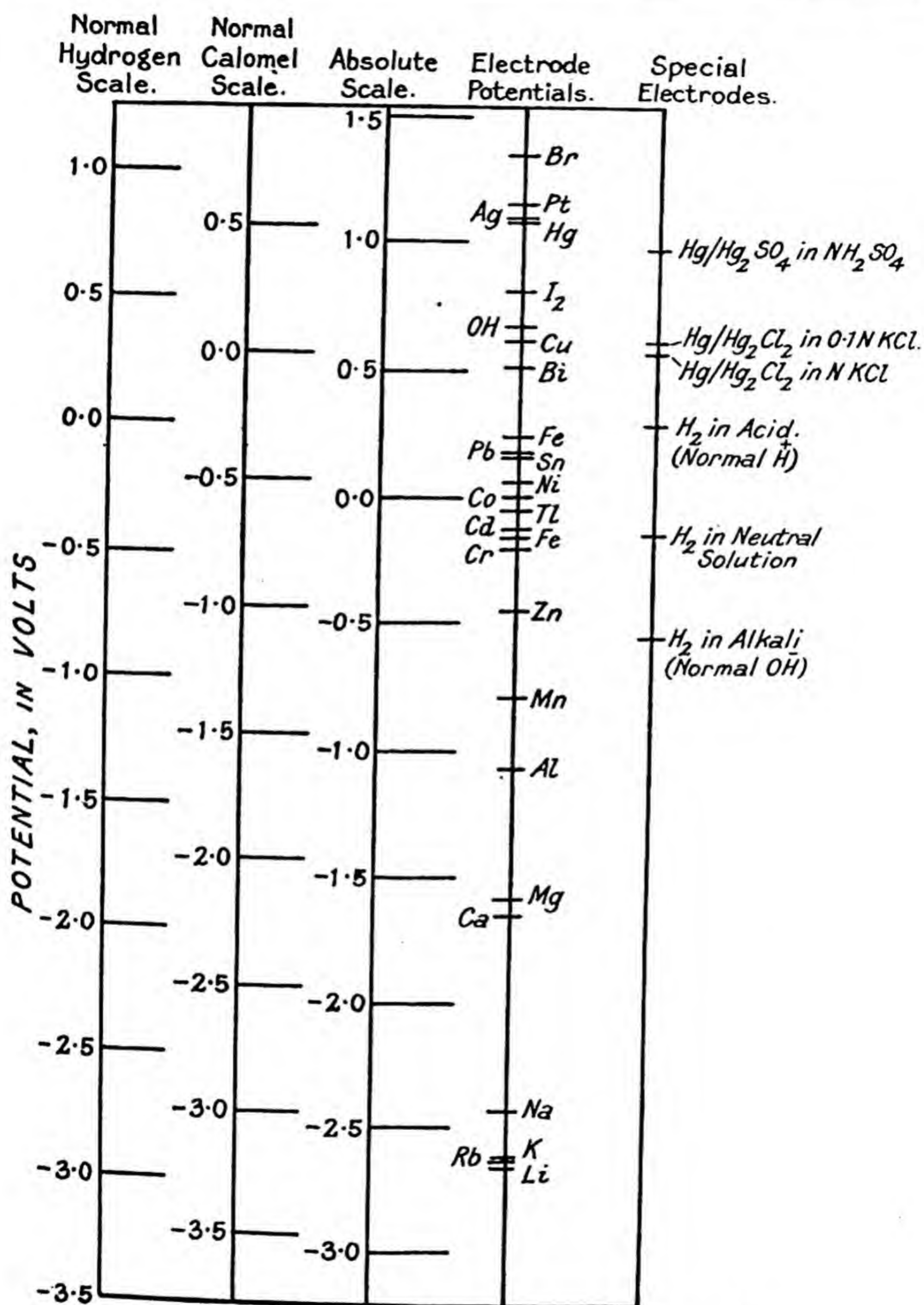
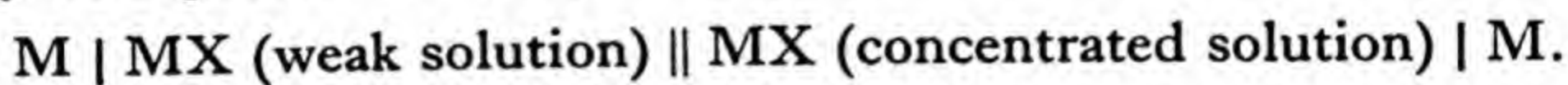


FIG. 26.—Normal electrode potentials on different scales.

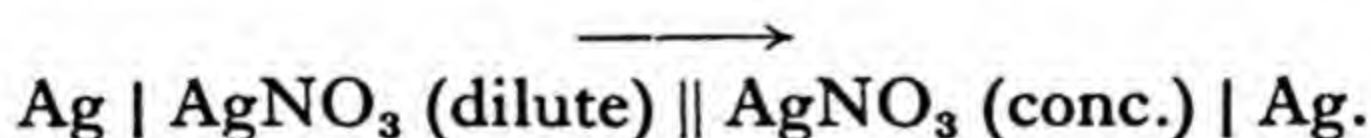
neglected, or it may be determined experimentally by special measurements in suitable diffusion cells. In this way absolute values of π_2 , the electrode potentials in any non-aqueous solution, may be found. Except for the work of Buckley and Hartley, existing data do not suffice for any accurate and extensive calculation of standard electrode potentials in solvents other than water.

86. Concentration cells.—In the Daniell cell an electromotive force is obtained when two dissimilar metals are immersed in different electrolytes, but there are other types of cells in which the electrodes are composed of the same metal dipping, either in different electrolytes, or in the same electrolyte at different concentrations. Now the potential difference at a metal-solution interface depends upon the concentration of the metal ions in the solution, and if we use different ionic concentrations about the two electrodes of the same metal, it is evident that there will be, on the whole, a potential difference between the electrodes. This arrangement is known as a *concentration cell*. The electrical energy does not come from chemical reactions, but from the energy of expansion, as the solute passes from the more to the less concentrated parts of the electrolyte.

There are two types of concentration cells, the first of which may be represented thus,



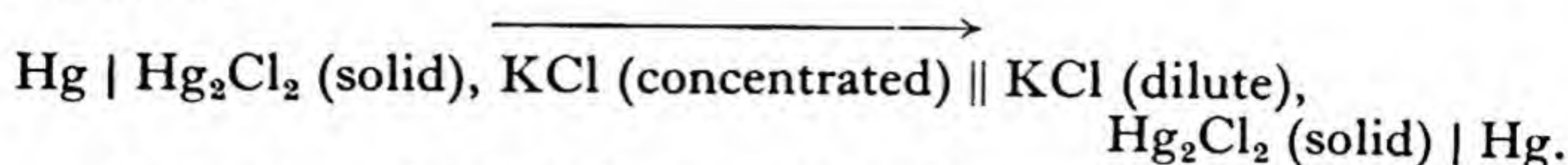
It consists of two reversible electrodes in equilibrium with solutions at different concentrations, the solutions being actually in contact or connected by a liquid junction. Cells of this type are known as *concentration cells with transference*. One such cell is



The electrode in contact with the more concentrated solution attains, at the equilibrium state, a higher positive potential than the other. When one faraday of electricity passes, one gram-equivalent of silver is deposited at the kathode, and n_A moles of salt represent the gain in concentration of the solution around the anode,* the electrolyte in the vicinity of the kathode losing an equal amount. Thus the electromotive force of this cell depends upon the transference number for the anion.

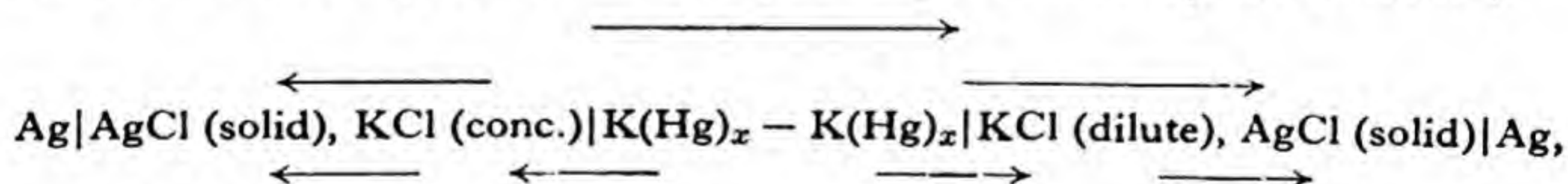
* See Section 46.

A second type of concentration cell with transference is of the form,

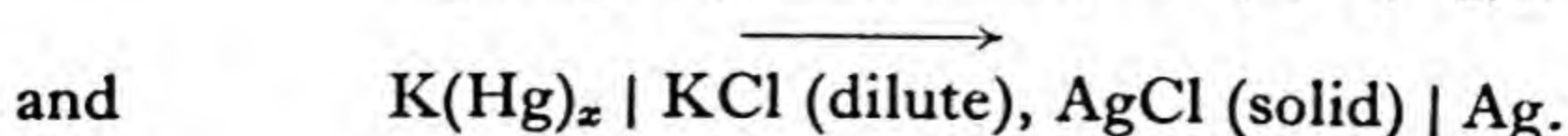
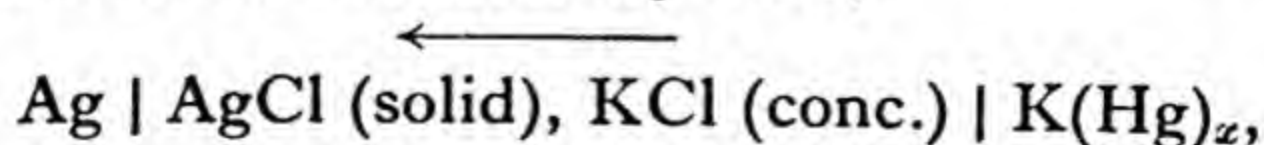


Mercurous chloride is very insoluble, so that the mass of it dissolved, which alone is electrolytically active, is constant, and the two mercury junctions are always maintained in the same condition. When a faraday of electricity passes through the cell from left to right a gram-equivalent of mercury dissolves at the first electrode, and displaces some of the mercury in the chloride. The mercury thus liberated forms fresh mercurous chloride with an equivalent of the chloride ions from the potassium chloride. A mole of the latter is thus removed from the concentrated solution. Meanwhile, at the other end of the chain, mercury is deposited from the mercurous chloride and a mole of potassium chloride must, therefore, appear in the more dilute solution. The chloride ions meanwhile have been migrating against the current from the dilute to the concentrated solutions, this process involving a loss of n_A moles of salt at the kathode. The dilute solution therefore, on the whole, only gains $1 - n_A$ moles, the concentrated solution losing an equal amount. Since $1 - n_A = n_K$, where n_K is the kation transference number, the action of this type of cell depends upon the transference number for the kation.

The second class of concentration cell does not involve the effects of migration and is known, therefore, as a *concentration cell without transference*. It may be represented by the scheme,



where K(Hg)_x represents a potassium amalgam. There is no migration from one solution of potassium chloride to the other, but an increase in the amount of silver chloride in the first half cell and a decrease in the second half. Since silver chloride is very insoluble, its dissolved mass remains constant and the silver electrodes remain in the same state. We may suppose the cell to be composed of two elementary cells,



When one faraday of electricity passes through the cell from left to right, one gram molecule of salt is formed in the dilute solution, and decomposed in the more concentrated solution. The result, therefore, is not complicated by migration effects.

The difficulty with this type of cell is to find electrodes which are reversible for both ions of the electrolyte.

87. Thermodynamics of concentration cells.—The thermodynamic relations connecting the osmotic work and the electrical energy* for the two kinds of concentration cells may be derived by the use of the thermodynamic engine, devised by Washburn.† Fig. 27 (a) represents the engine used for the cell

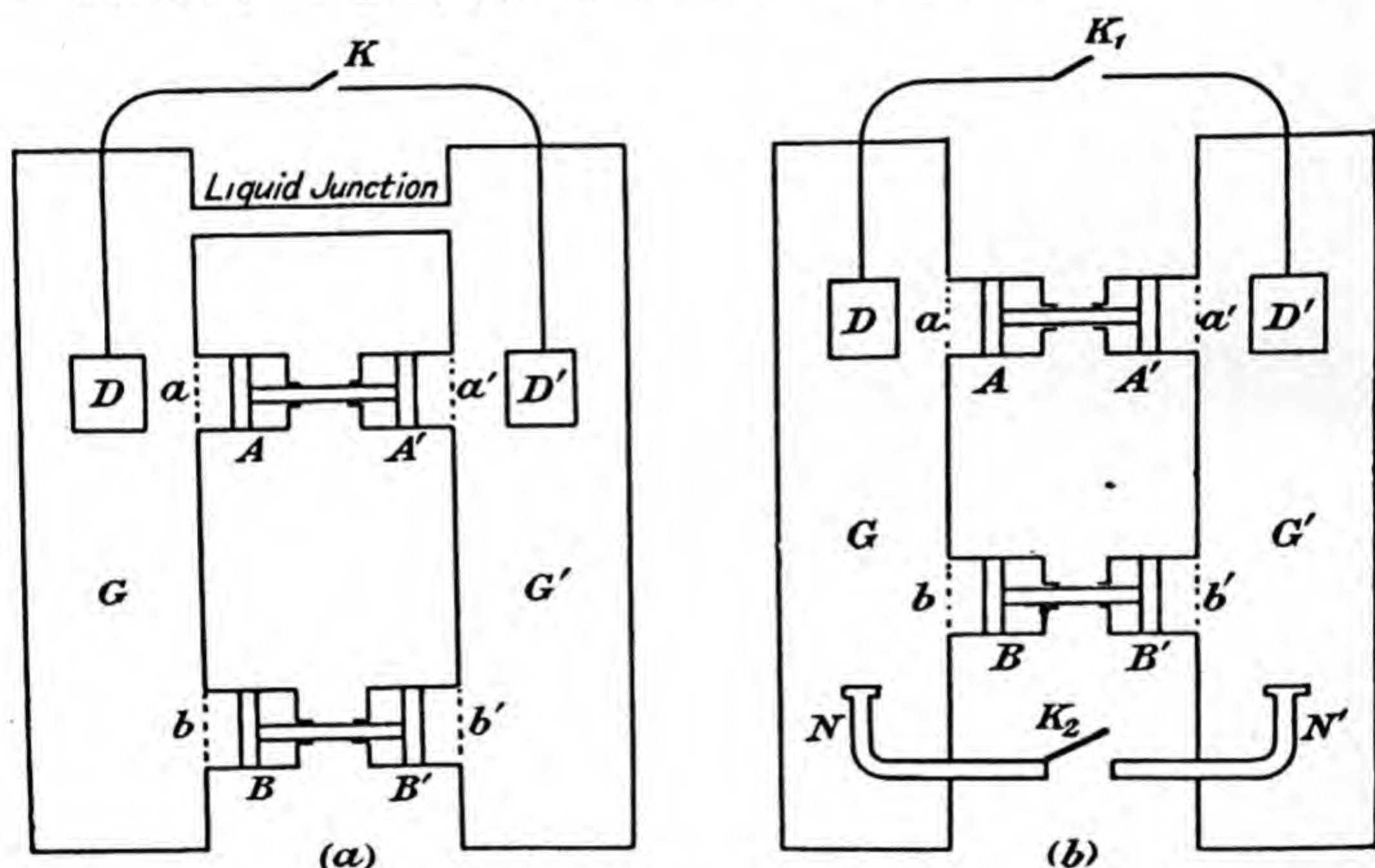


FIG. 27.—A thermodynamic engine.

with transference. A chamber, G, contains the salt solution, MX, at concentration C , the osmotic pressures of the ions at this concentration being represented by P_M and P_X . D is a reversible electrode, and the cylinder A is fitted at one end with a membrane, a , permeable only to the M ion. The piston in the cylinder permits the passage of water only, and the solution between the piston and the membrane consists, therefore, of a solution of M ions in osmotic equilibrium with the solution in the chamber G. The membrane b is permeable only to X ions.

* See MacInnes and Parker, *Jour. Amer. Chem. Soc.*, 37, 1445 (1915).

† *Ibid.*, 32, 467 (1910).

The other half of the engine is similar to that just described, except that the vessel G' contains the salt at the concentration $C + \delta C$ and the ions have the osmotic pressures $P_M + \delta P_M$ and $P_X + \delta P_X$. A movement of the piston A, A' from the left to the right is obviously against the osmotic pressure δP_M . An electrolytic connection with the vessel G to G' is afforded by the liquid junction shown.

If the key K is closed, and one faraday of electricity is allowed to pass, one gram-equivalent of X ion will be formed at the electrode D , and a like amount will be removed from the solution by electrolysis at the electrode D' . The passage of the electricity across the liquid junction will be accompanied by the movement of n_K equivalents of M ions in the direction of the current—from G' to G —and the migration of $(1 - n_K)$ equivalents of X ions in the reverse direction, where n_K is the kation transference number. Thus the total effect of the operations in the cell will be the transfer of n_K equivalents of MX from the solution of concentration $C + \delta C$ to that of concentration C . To compensate for this change, and to maintain a constant difference of concentration, the pistons A, A' and B, B' are moved reversibly towards the right, withdrawing n_K moles of each ion from the chamber G , and forcing them into G' . As the electrical energy must be equal to the osmotic work, the following relation holds,

$$F\delta E = n_K(v_M\delta P_M + v_X\delta P_X), \quad (116)$$

where E is the E.M.F. of the cell and v_M, v_X , the volumes of the solution containing one gram-equivalent of ion.

Fig. 27 (*b*) represents the thermodynamic engine for cells without transference. It is similar to that shown in (*a*), except that the liquid junction has been replaced by electrodes, N, N' , such as amalgam electrodes. The concentrations of the salt are as before C and $C + \delta C$, respectively, in the chambers G and G' . On closing the keys K_1 and K_2 and allowing one faraday to pass, one gram-equivalent both of the M and X ions will be formed in the chamber G , and a like amount will be removed by the electrodes from G' . To maintain equilibrium, the pistons A, A' , and B, B' must be moved reversibly towards the right, each through a volume containing one equivalent of ion. Equating the osmotic work and the electrical energy, we have

$$F\delta E = v_M\delta P_M + v_X\delta P_X, \quad (117)$$

an expression which differs from equation (116) only in the fact that it does not contain the transference number n_K .

If each molecule of the electrolyte is capable of dissociating

into y_M kations, and y_X anions, of valencies ν_M and ν_X , respectively, then,

$$v_M = \frac{v}{y_M \nu_M} \text{ and } v_X = \frac{v}{y_X \nu_X},$$

where $y_M \nu_M$ is equal to $y_X \nu_X$, and v is the volume of the solution containing one mole of completely ionised electrolyte. Also the osmotic pressures are given by

$$P_M = y_M CRT \text{ and } P_X = y_X CRT,$$

where $C = \frac{1}{v}$, so that from equation (117),

$$F \delta E = \frac{y_M + y_X}{y_M \nu_M} \cdot RT \frac{\delta C}{C}.$$

On integration,
$$E = \frac{nRT}{\nu F} \log \frac{[C_1]}{[C_2]}, \quad (118)$$

n being the total number of ions into which one molecule of the salt may dissociate, ν , the total valency of the anions, or of the kations, obtained from one molecule, and $\frac{[C_1]}{[C_2]}$ is the ratio of the concentrations of the ions in the two solutions.

If the molecule yields two ions, each of valency ν , then,

$$E = \frac{2RT}{\nu F} \log \frac{[C_1]}{[C_2]}. \quad (119)$$

Similarly, assuming that n_K is independent of the concentration, we have, on integrating equation (116),

$$E = \frac{n_K n RT}{\nu F} \log \frac{[C_1]}{[C_2]}, \quad (120)$$

i.e.,
$$E = \frac{u_K}{u_K + u_A} \cdot \frac{nRT}{\nu F} \log \frac{[C_1]}{[C_2]},$$

and for the cell where the electromotive force involves the anion transference number,

$$E = \frac{u_A}{u_K + u_A} \cdot \frac{nRT}{\nu F} \log \frac{[C_1]}{[C_2]}. \quad (121)$$

We may also derive equation (120) in the following manner. Let p represent the electrolytic solution pressure, the same for both electrodes, ν , the valence of the metal, P_1 and $[C_1]$, the osmotic pressure, and concentration of the ions, respectively, in the more dilute solution, P_2 and $[C_2]$ being the corresponding quantities

for the concentrated solution. Then if π_1 , π_{12} , π_2 , represent the potential differences at the first metal-solution interface, the dilute-concentrated solution interface, and the second metal-solution interface, respectively,

$$E = \pi_1 + \pi_{12} + \pi_2.$$

But from equation (110),

$$\pi_1 + \pi_2 = \frac{RT}{\nu F} \left(\log \frac{P_1}{p} - \log \frac{P_2}{p} \right),$$

and taking the osmotic pressures as being proportional to the ionic concentrations,

$$\pi_1 + \pi_2 = \frac{RT}{\nu F} \log \frac{[C_1]}{[C_2]}. \quad (122)$$

Also in section (91) it is shown that π_{12} is equal to

$$\frac{u_K - u_A}{u_K + u_A} \cdot \frac{RT}{\nu F} \log \frac{[C_1]}{[C_2]}. \quad (123)$$

Thus, if the molecule yields two ions, each of valency ν ,

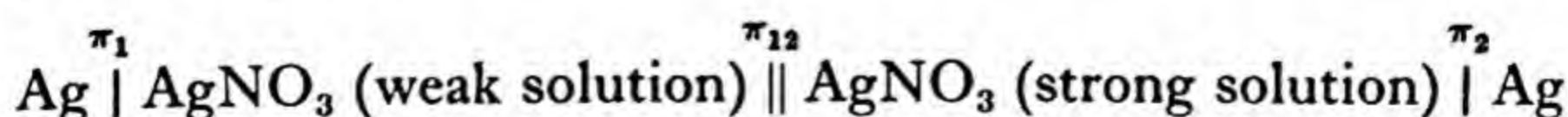
$$E = \frac{2u_K}{u_K + u_A} \cdot \frac{RT}{\nu F} \log \frac{[C_1]}{[C_2]}. \quad (124)$$

Since $\frac{u_K}{u_K + u_A} = n_K$, equation (120) follows immediately. A similar expression involving n_A can be obtained for those cells of which the electromotive force involves the anion transference number.

In the case of cells without transference, since the migration effects are eliminated, n_K is unity. Hence from equations (122) and (123),

$$E = \frac{2RT}{\nu F} \log \frac{[C_1]}{[C_2]}.$$

88. Concentration cells with transference.—In this particular type of cell there is a small potential difference at the liquid-liquid interface which, in some cases, may be neglected. For example, in the cell



there is a tendency for the Ag^+ and NO_3^- ions to diffuse from the concentrated to the dilute solutions, but the NO_3^- ion has the greater mobility and consequently diffuses more quickly, so that

after a short time a relative excess of nitrate ions will have crossed the junction, and the weaker solution will have, consequently, a negative charge. The strong solution contains, on the whole, an excess of Ag^+ ions, and, therefore, the electrostatic field set up will equalise the rates of diffusion for the positive and negative ions, since it will accelerate the silver ions and retard the nitrate ions. The concentrated solution will be positive with respect to the dilute solution and therefore the E.M.F. of the cell is given by

$$E = \pi_2 + \pi_{12} - \pi_1.$$

The hydrogen ion has a greater velocity than other ions, and therefore with acids the *dilute* solution is *positive* with respect to the more concentrated one. In alkalis the hydroxyl ion moves faster than the associated metallic ion, and the *concentrated* solution is *positive* with respect to the dilute one. If the two ions possess equal velocities, as they do, approximately, in potassium chloride solutions, there is no liquid-junction potential difference. The latter, if present, may be eliminated by mixing with both solutions a strong neutral electrolyte. In this case most of the current is carried by the ions of this neutral electrolyte.

Abegg and Cumming * eliminated the effect by interposing a concentrated solution of a salt between the two liquids. They used ammonium nitrate with the silver nitrate cell, and since their calculated and observed values of the E.M.F. agreed, it is evident that the liquid-junction potential difference was practically eliminated. They also employed saturated solutions of potassium nitrate and of potassium chloride as the so-called "bridge." Schatchard † has shown that in a hydrochloric acid concentration cell, the liquid-liquid junction potential difference is not more than one milli-volt, provided that the solutions have concentrations less than 0.1 normal, and a saturated potassium chloride solution is interposed between the two acid solutions.

A common form of cell ‡ is shown in Fig. 28. The vessels M, M' contain identical silver-silver chloride electrodes, made by depositing silver electrolytically on fine platinum wire, and then covering the silver with a deposit of silver chloride. The tubes L, L' are brought together in a small vessel K, which contains a solution formed by mixing together equal parts of the solutions contained in M and M'.

The electromotive forces may be calculated from equation (121).

* *Zeits. Elektroch.*, **13**, 17 (1907).

† *Jour. Amer. Chem. Soc.*, **45**, 1719 (1923).

‡ See MacInnes and Parker, *loc. cit.*

If Λ_1 and Λ_2 are the equivalent conductances of the two solutions, α_1 and α_2 , their degrees of ionisation, then,

$$\frac{[C_1]}{[C_2]} = \frac{\alpha_1 C_1}{\alpha_2 C_2} = \frac{\Lambda_1 C_1}{\Lambda_2 C_2} \quad (125)$$

where C_1 and C_2 are the concentrations of the solutions. MacInnes and Parker determined, experimentally, the E.M.F.

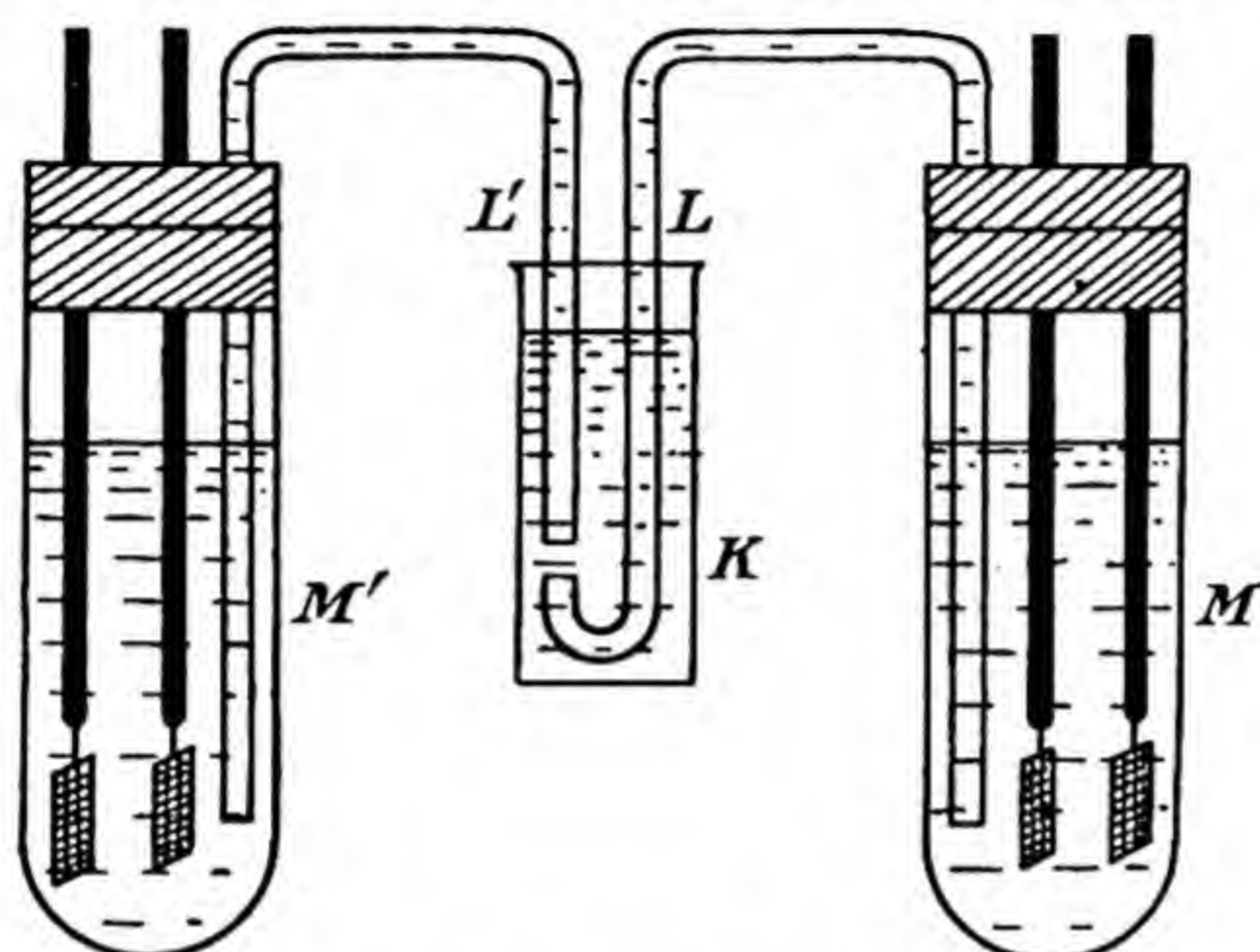


FIG. 28.—Concentration cell with transference.

of potassium chloride cells at 25° C. Their results, together with those calculated by means of equations (121) and (125), were as follows :—

Ag AgCl (solid), KCl KCl, AgCl (solid) Ag.						Calculated E.M.F. Volt.	Observed E.M.F. Volt.
"	"	0.5N	0.05N	"	"	0.05562	0.05357
"	"	0.1N	0.01N	"	"	0.05647	0.05400
"	"	0.05N	0.005N	"	"	0.05690	0.05470
"	"	0.01N	0.001N	"	"	0.05775	0.05600

It will be observed that the experimentally determined values are lower than the calculated ones. In other words, the ratio of the number of ions in the two solutions, as calculated from electromotive force measurements, do not agree with that obtained from conductance measurements. This discrepancy is also illustrated in the following table, the measurements being made at 25° C.*

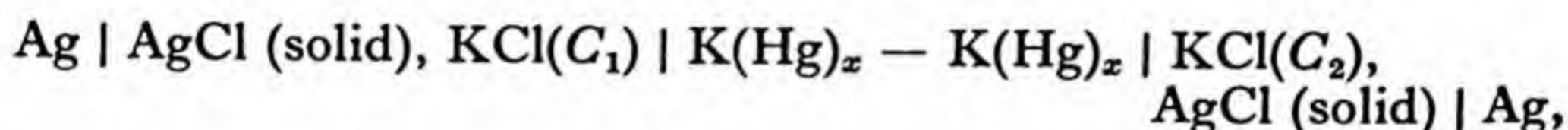
It may be that the degree of ionisation, α , is not correctly given by the ratio $\frac{\Lambda}{\Lambda_0}$, in which case it is impossible to calculate

* See MacInnes and Parker, *loc. cit.*

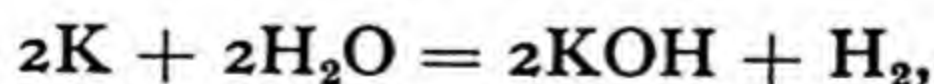
Ag AgCl (solid), HCl(C ₁) HCl(C ₂), AgCl (solid) Ag.				Hg Hg ₂ Cl ₂ , KCl(C ₁) KCl(C ₂), Hg ₂ Cl ₂ Hg.			
Values of		$\frac{[C_1]}{[C_2]}$ from E.M.F. Measure- ments.	$\frac{[C_1]}{[C_2]}$ from Conduct- ance Measure- ments.	Values of		$\frac{[C_1]}{[C_2]}$ from E.M.F. Measure- ments.	$\frac{[C_1]}{[C_2]}$ from Conduct- ance Measure- ments.
C ₁ .	C ₂ .			C ₁ .	C ₂ .		
0.1N	0.02N	4.57	4.78	0.5N	0.05N	8.09	8.85
0.1N	0.01N	8.82	9.49	0.1N	0.01N	8.33	9.16
0.1N	0.002N	41.80	46.70	0.05N	0.005N	8.64	9.30
				0.01N	0.001N	9.04	9.62

the electromotive force of any cell from conductance measurements. If the potential difference at the junction of the two solutions is not negligible, another source of error is introduced, since these potential differences evade direct measurement, complete elimination or correct calculation.

89. Concentration cells without transference.—These cells involve two sets of reversible electrodes as, for example, silver chloride and reversible amalgam electrodes. The form of apparatus which must be employed is also complicated. Thus, to measure the electromotive force of the cell,



MacInnes and Parker used the apparatus shown in Fig. 29, where R, E, R', E' represent the silver chloride electrodes, consisting of pieces of platinum gauze plated with a thick coating of silver, on which silver chloride was deposited. The alkali metal amalgam electrode had two capillary outlets, J and J', for the amalgam, so that it could be used in either of the two half cells. There is a side reaction in this type of cell as follows:—



and to overcome this, a constantly flowing amalgam was employed. The arrangement of the cell also permitted the immediate removal of the amalgam drops as they became detached, since they fell directly into the bulb D, and thence to the residue flask. Streams of fresh solution run in through tubes G and G' were made to pass by the electrodes; this ensured that the measurements were carried out with solutions uncontaminated by the

passage of the amalgam. The separation of each half-cell into two portions, CK, C'K', made it possible to leave the silver-silver chloride electrodes in contact with the solution with which they were in equilibrium, this state being undisturbed by the solution flowing past the amalgam electrodes. The bent connecting tubes prevented mixing.

With potassium chloride solutions, 0.5 and 0.005 normal,

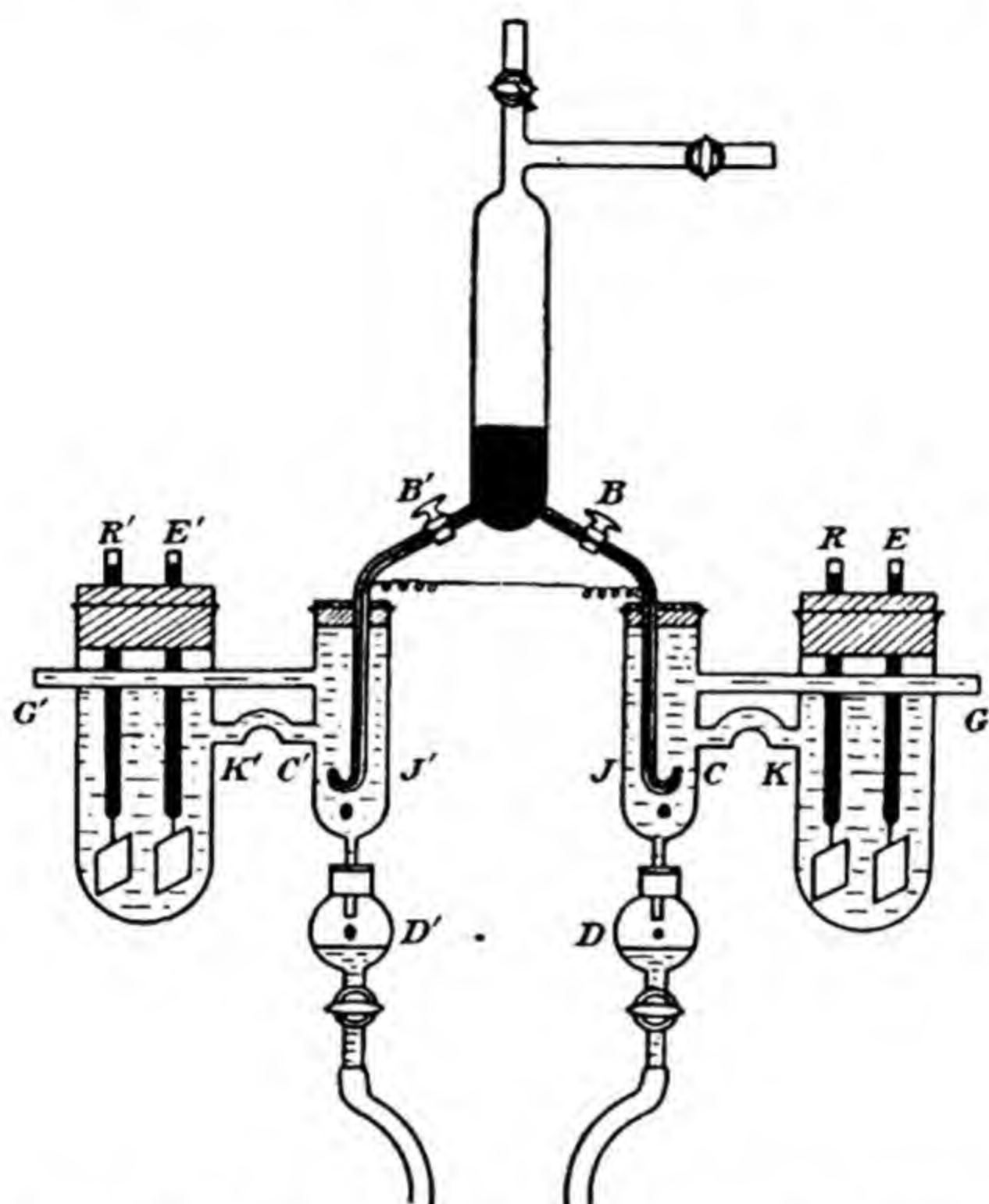


FIG. 29.—Concentration cell without transference.

the E.M.F. of the cell, with widely varying concentration of the amalgam electrode, was as follows :—

Concentration of amalgam	0.02 per cent.	0.002 per cent.	0.0002 per cent.
E.M.F. of cell (volt)	0.10603 ± 0.00001	0.10600 ± 0.00001	0.1060 ± 0.0005

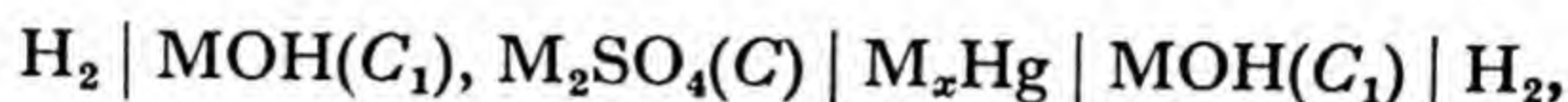
These results indicate that within wide limits the electromotive force is independent of the amalgam concentration. Values of the E.M.F. for different concentrations of the potassium chloride solutions are given in Table LIII. :—

TABLE LIII.

ELECTROMOTIVE FORCE OF KCl CELLS WITHOUT TRANSFERENCE AT 25° C.

←				→		E.M.F. Volts.
Ag AgCl (solid), KCl K _x Hg	Per cent.	—	K _x Hg KCl, AgCl (solid) Ag.			
" " 0.05N	.02		0.5N " "		0.10735	
" " 0.05N	.002		0.5N " "		0.10745	
" " 0.01N	.004		0.1N " "		0.10885	
" " 0.01N	.002		0.1N " "		0.10900	
" " 0.005N	.004		0.05N " "		0.11085	
" " 0.005N	.002		0.05N " "		0.11085	

Another form of vessel is that used by Akerlöf * in his experiments with the cell,



where M represents lithium, sodium or potassium, shown diagrammatically in Fig. 30. Its great advantage lies in the fact that it can be thoroughly washed and filled with a solution, without removal from the thermostat. In working with the cell, approximately the required amount of water was placed in A, boiled under vacuum and then weighed. The amount of alkali hydroxide solution which, when added to this water, would give a solution of approximately the desired strength, was run in. At first, all of the stopcocks except 4, 4 and 5, 5 were closed, and the system exhausted to a low pressure. Then, in succession, stopcocks 3, 3 were opened, 5, 5 closed, 1, 1 opened and the apparatus filled with the solution. After this, stopcocks 1, 1 and 4, 4 were closed and 8, 8, which were connected to the hydrogen supply, opened. In the next series of operations C was opened to the atmosphere and 5, 5 opened until the solutions in the hydrogen electrode compartments, B, B', were at suitable levels. Hydrogen was then introduced through 7, 7, until the hydrogen electrodes had attained equilibrium. Afterwards, taps 9 and 10 were opened, and hydrogen passed over the amalgam. The taps 6, 6 were then opened completely, and the amalgam which flowed into the bottom of the tubes was removed, as rapidly as it entered, through the taps 5, 5. This flow was adjusted by hand and care was taken to keep the levels of the solutions in the hydrogen electrode compartments constant. In an experiment the tube D, which contained, approximately, 30 c.c. of amalgam, emptied in 10 minutes. During this time as many readings as possible were taken, and the mean of these taken as the electromotive force of the cell.

* *Jour. Amer. Chem. Soc.*, 48, 1160 (1926).

A simpler type of cell is that used by Wolfenden, Wright, Kane and Buckley,* shown in Fig. 31. The right-hand limb, A,

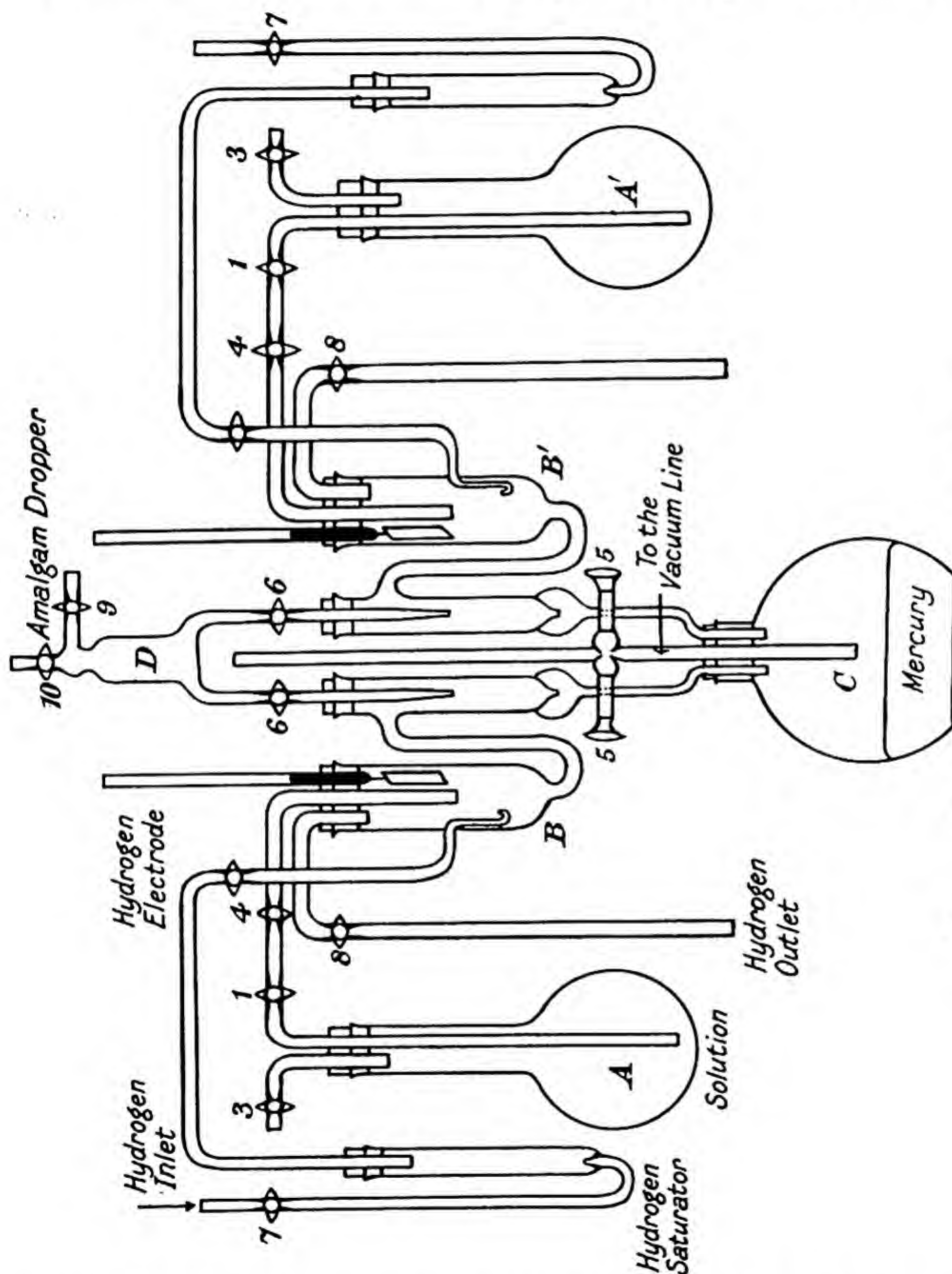


FIG. 30.—Concentration cell without transference.

contains a pair of silver-silver chloride electrodes, and the left limb, B, the streaming amalgam electrode. The volume of A is

* *Trans. Farad. Soc.*, **23**, 493 (1927).

about 40 c.c., while B has a capacity of 3 or 4 c.c. to ensure the most rapid rate of renewal of the solution round the amalgam

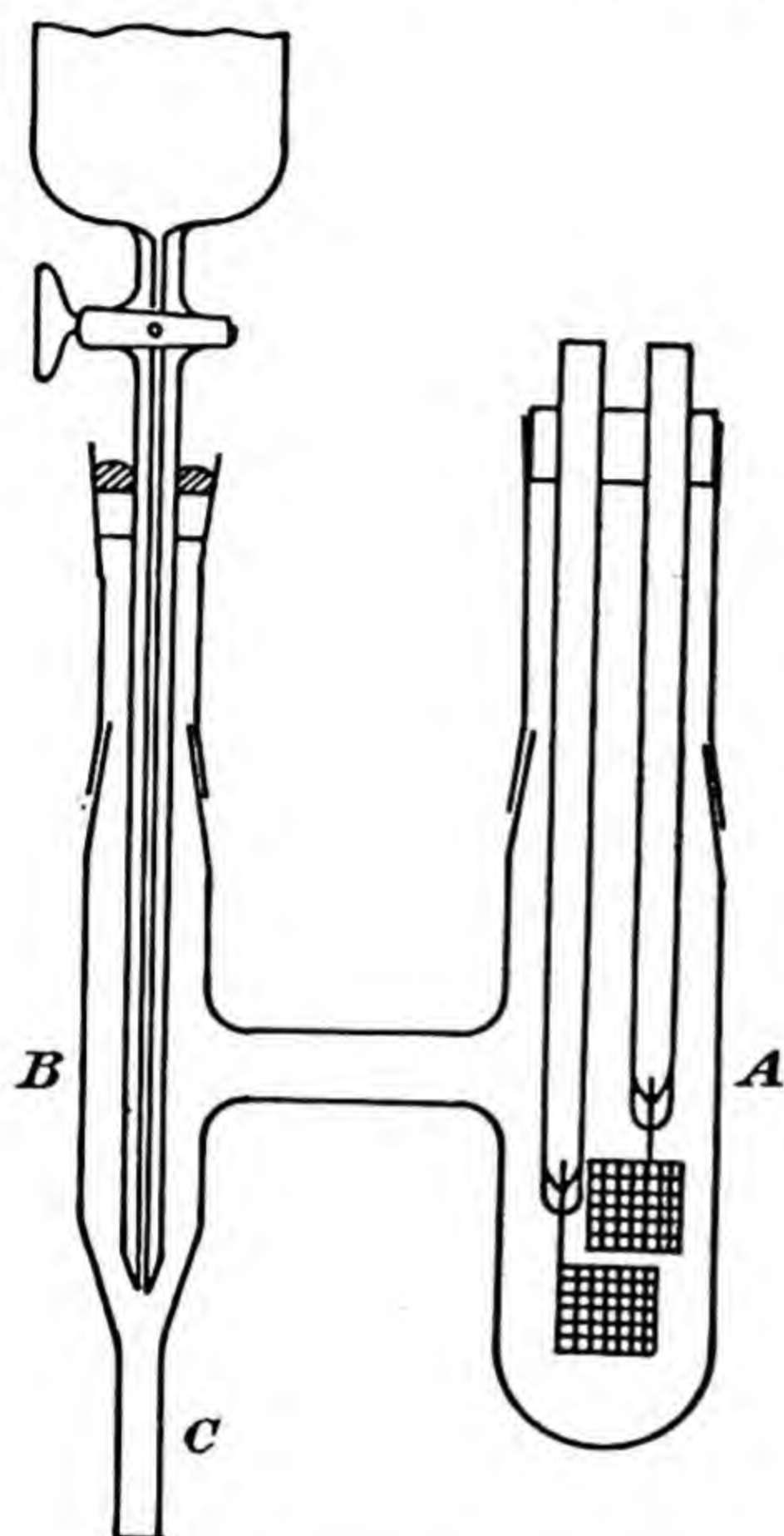


FIG. 31.—Amalgam half-cell.

tip, for a given expenditure of solution. If the left limb has as large a capacity as that on the right, decomposition is so fast as to cause the electromotive force to drop steadily, at a rate dependent upon the dilution of the solution. For similar reasons, the amalgam tip is ground to a conical form, and placed at a point where the solution stream approaches its maximum velocity. With the form of cell illustrated, the experimenters found that there was no decrease in the value of the electromotive force with time, and the value did not vary appreciably with the rate of flow of the solution. The latter entered B from behind, at a point just above the amalgam tip, and both solution and amalgam left the cell at C.

90. Measurement of the electromotive force of a concentration cell. —

The electromotive force of a concentration cell is always measured by means of the potentiometer method. Various elaborate potentiometers are now in use, but the arrangement shown in Fig 32 indicates the principle employed in all electromotive force measurements.*

A is a large 2-volt accumulator and B a variable resistance. A potentiometer measuring wire, CD, is fitted with a slider and scale. It is convenient to construct a coil of wire E so that its resistance between the points ee' is exactly 101.93 times that of the slide wire CD, the electromotive force of the standard cell F being taken as 1.0193 volts. G is the concentration cell, and H a double change-over switch by means of which the galvanometer, or the electrometer, K can be thrown, either into the measuring

* See Grant, *Trans. Farad. Soc.*, 20, 385 (1924).

circuit CGM, or into the standard cell circuit $ee'F$. L is a short-circuiting key for the electrometer. In taking a measurement the current through E and CD is altered by means of B , so that there is no deflection in the galvanometer when F is connected across ee' , the potential difference between these points being then equal to 1.0193 volts. Immediately afterwards, the cell

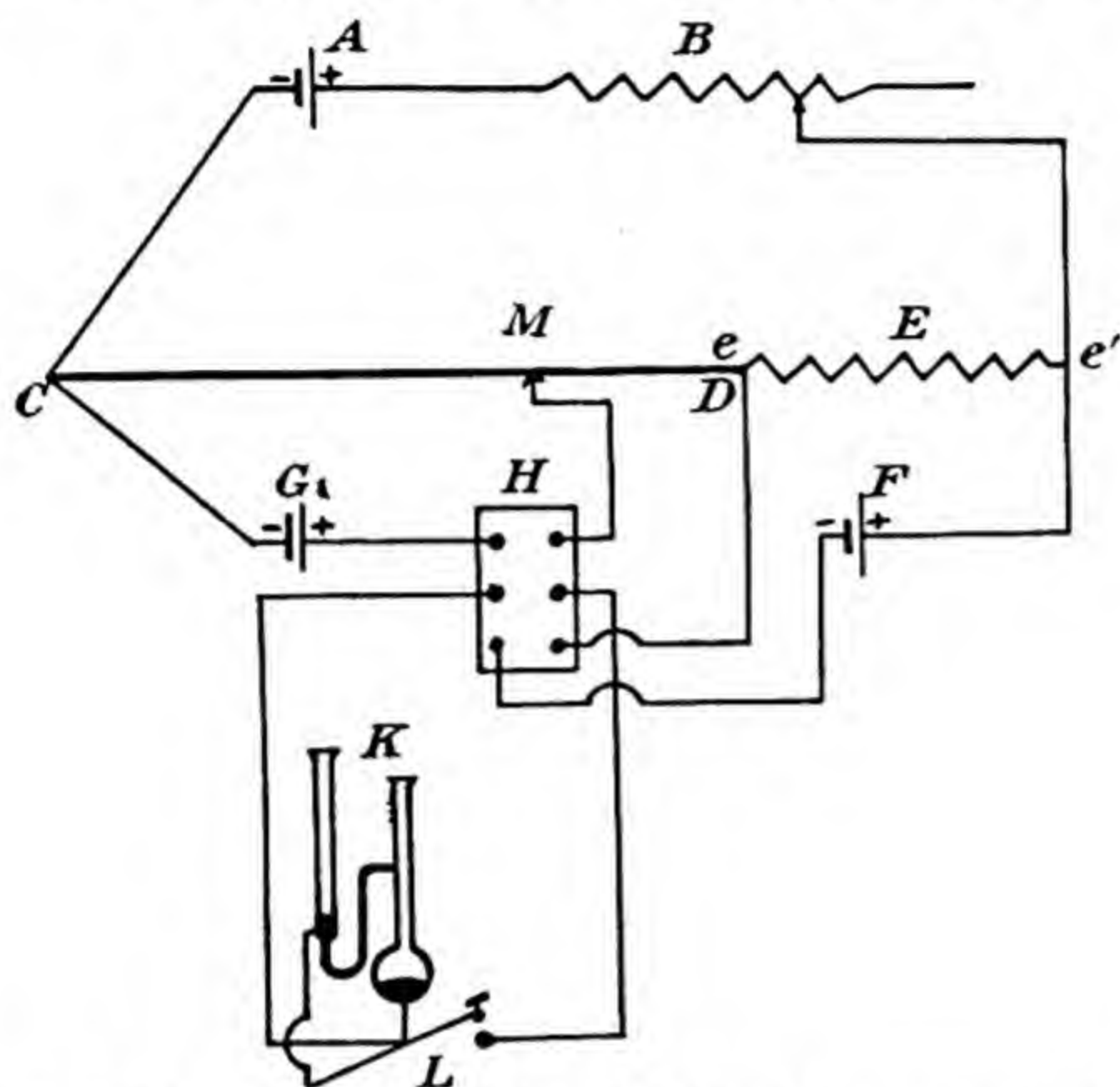


FIG. 32.—Measurement of the E.M.F. of concentration cells.

G is balanced against the potential difference between C and M by moving the sliding contact M . Then, since the current through CD and E remains constant during these two operations,

$$\frac{\text{E.M.F. of } G}{1.0193} = \frac{\text{potential difference between } CM}{\text{potential difference across } ee'} \\ = \frac{\text{resistance of } CM}{\text{resistance of } E} = \frac{CM}{CD \times 101.93},$$

$$\text{and therefore E.M.F. of the concentration cell} = \frac{CM}{CD} \times \frac{1}{100} \text{ volts,}$$

where CM and CD refer to the lengths of the wire between these points. As mentioned previously many very sensitive types of potentiometers are now in use, but the principle remains the same. The most sensitive types measure to the nearest microvolt, or even less.

91. Liquid-liquid potentials.—A concentration cell with transference will give an electromotive force which is the algebraic

sum of three potential differences: those at the two electrodes plus that at the junction of the solutions. Since, for many theoretical purposes, the potential difference at the electrodes alone is desired, many attempts have been made to eliminate, or evaluate, the liquid-junction potential difference. Nernst* suggested that for the same salt solution, at different concentrations, containing equi-valent ions of valency ν , it could be calculated in the following manner. Let the osmotic pressure of each set of ions in the two solutions be P_1 and P_2 , respectively. If ν faradays, *i.e.*, νF coulombs, of electricity pass across the junction in the direction

from the dilute to the concentrated solution, $\frac{u_K}{u_K + u_A}$ gram ions

of metal are transferred in this direction, and $\frac{u_A}{u_K + u_A}$ gram ions

of the anion in the opposite direction, where u_K and u_A are the velocities of the kation and anion, respectively. Hence the energy expended in the case of the metal ions is, from section (77),

$\frac{u_K}{u_K + u_A} RT \log \frac{P_1}{P_2}$, and that expended during the transfer of the

anions is $-\frac{u_A}{u_K + u_A} RT \log \frac{P_1}{P_2}$. But the total electrical work

done in transferring ν faradays across the junction is $\nu F \pi$, where π is the liquid-junction potential difference. Hence,

$$\pi = \frac{u_K - u_A}{u_K + u_A} \frac{RT}{\nu F} \log \frac{P_1}{P_2} = \frac{u_K - u_A}{u_K + u_A} \frac{RT}{\nu F} \log \frac{[C_1]}{[C_2]}, \quad (126)$$

where $[C_1]$ and $[C_2]$ are the ionic concentrations corresponding to the osmotic pressures, P_1 and P_2 . If α_1, α_2 are the degrees of dissociation, C_1, C_2 the solution concentrations, and Λ_1, Λ_2 the equivalent conductances of the two solutions, then,

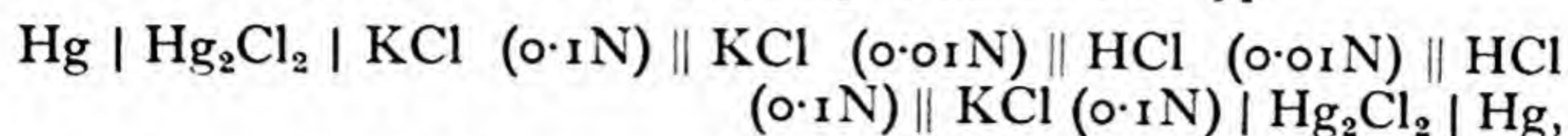
$$\pi = \frac{u_K - u_A}{u_K + u_A} \frac{RT}{\nu F} \log \frac{\Lambda_1 C_1}{\Lambda_2 C_2}.$$

It will be noted that, since the potential difference depends upon the ratio of the concentrations of the two sets of ions, and not upon the absolute values, the potential difference at a junction such as HCl (0.1N) | KCl (0.1N) should be equal to that at the junction KCl (0.01N) | HCl (0.01N), but of opposite sign.† Nernst deter-

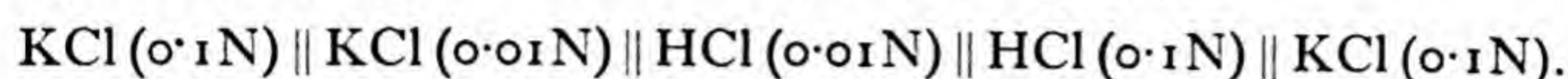
* *Zeits. phys. Chem.*, 2, 613 (1888); 4, 129 (1889).

† This assumes that the ratio of the degrees of dissociation is the same in the two cases.

mined the potential difference, at 18° C., at the junctions of several electrolytic solutions, using cells of the type



in which, since the two potential differences at the electrodes are equal, the measured values are those of the junctions



His results are shown in Table LIV., in which u_A, u_K refer to one electrolyte, and u_A', u_K' to the other :—

TABLE LIV.

LIQUID-LIQUID JUNCTION POTENTIAL DIFFERENCES.

Electrolytes.	$\frac{u_K - u_A}{u_K + u_A} - \frac{u'_K - u'_A}{u'_K + u'_A}$	π (Observed) Volt.	π (Calculated) Volt.
KCl, NaCl	+ .237	.0111	.0137
KCl, LiCl	+ .366	.0183	.0211
KCl, NH ₄ Cl	+ .019	.0004	.0011
NH ₄ Cl, NaCl	+ .218	.0098	.0126
KCl, HCl	— .688	— .0357	— .0397
KCl, HNO ₃	— .719	— .0378	— .0414

In the general case, where the two solutions contain electrolytes at ionic concentrations $[C_1]$ and $[C_2]$, and the kations have, respectively, velocities u_K and u_K' , valencies ν_1 and ν_2 , and of which the anions have velocities u_A and u_A' , and valencies ν_1' and ν_2' , Henderson * proposed the formula,

$$\pi = \frac{RT}{F} \cdot \frac{(u_K - u_A)[C_1] - (u_K' - u_A')[C_2]}{(u_K\nu_1 + u_A\nu_1')[C_1] - (u_K'\nu_2 + u_A'\nu_2')[C_2]} \log \frac{(u_K\nu_1 + u_A\nu_1')[C_1]}{(u_K'\nu_2 + u_A'\nu_2')[C_2]} \quad (127)$$

When the solutions contain the same uni-univalent salts this reduces to equation (126),† and if the solutions have the same ionic concentration, and all the ions are univalent, then,

$$\pi = \frac{RT}{F} \frac{(u_K - u_K') - (u_A - u_A')}{(u_K - u_K') + (u_A - u_A')} \log \frac{(u_K + u_A)}{(u_K' + u_A')} \quad (128)$$

* *Zeits. phys. Chem.*, 59, 118 (1907); 63, 325 (1908).

† We assume that the ionic velocity is independent of concentration.

If, in addition, they have a common ion,

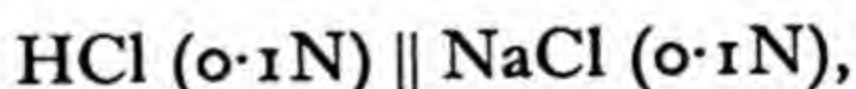
$$\pi = \frac{RT}{F} \log \frac{\Lambda}{\Lambda'}, \quad . \quad . \quad . \quad (129)$$

where Λ and Λ' are the equivalent conductances of the two solutions. For solutions of the same ionic concentration having a common univalent anion, combined with univalent and divalent kations, Henderson's formula reduces to

$$\pi = \frac{RT}{F} \frac{(u_K - u_{K'})}{(u_K - 2u_{K'})} \log \frac{(u_K + u_A)}{(2u_{K'} + u_A)}. \quad . \quad (130)$$

Henderson's formula appears to have a wide application, and represents experimental facts.

Planck * has also put forward a formula to represent the liquid-junction potential difference, which Lewis and Sargent † modified for a junction connecting two equally concentrated solutions of salts having a common ion. It takes the form of equation (129). Direct experiment shows that this formula may be relied upon to give values of the potential for this type of junction accurate to within 0.1 or 0.2 millivolt. Thus Buckley and Hartley ‡ measured the potential difference at the junction



the experimental value being 20.6 millivolts, and that calculated from equation (129), 20.2 millivolts. A similar cell containing 0.01 normal solutions gave experimental and calculated values of the potential differences equal to 17.85 and 17.9 millivolts, respectively.

MacInnes § has shown that the liquid-junction potential difference, π , is given by

$$\pi = \frac{E}{2} (2n_K - 1), \quad . \quad . \quad . \quad (131)$$

where E is the electromotive force of a cell without transference, containing the two solutions, and n_K is the transference number for the kation. For a cell with transference, of electromotive force E_t ,

$$\pi = \frac{E_t}{2n_K} (2n_K - 1), \quad . \quad . \quad . \quad (132)$$

* *Wied. Ann.*, **40**, 561 (1890).

† *Jour. Amer. Chem. Soc.*, **31**, 363 (1909).

‡ *Phil. Mag.*, **8**, 320 (1929).

§ *Jour. Amer. Chem. Soc.*, **37**, 2301 (1915).

and these formulæ are in accord with the most accurate measurements of the electromotive forces of concentration cells.

MacInnes and Yeh * measured the liquid-junction potential differences of 0.1 normal solutions of univalent chlorides at 25° C. and also calculated the values by means of equation (129). The close agreement between the calculated and observed values is shown in Table LV.

TABLE LV.

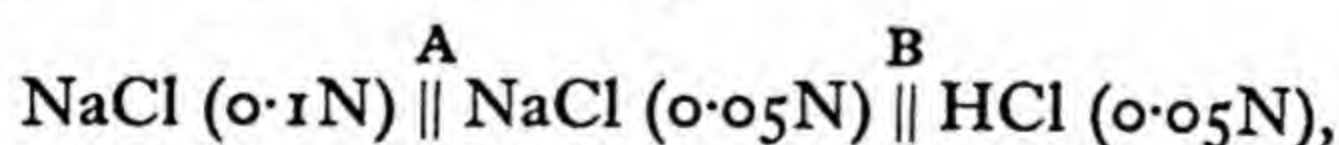
POTENTIAL DIFFERENCES AT THE JUNCTIONS OF 0.1N UNIVALENT CHLORIDES.

Electrolytes.	π (Millivolts).		Electrolytes.	π (Millivolts).	
	Measured.	Calculated.		Measured.	Calculated.
HCl, KCl	26.78	28.4	KCl, LiCl	8.79	7.4
HCl, NaCl	33.09	33.3	KCl, NH ₄ Cl	2.16	0.2
HCl, LiCl	34.86	35.8	NaCl, LiCl	2.62	2.5
HCl, NH ₄ Cl	28.40	28.6	NaCl, NH ₄ Cl	— 4.21	— 4.6
KCl, NaCl	6.45	4.9	LiCl, NH ₄ Cl	— 6.93	— 7.2

It will be noted that the junctions connecting differently concentrated solutions of two salts, with a common ion, may be replaced by two junctions, one of which joins solutions of the same salt at different concentrations, and the other connects solutions of different salts at the same concentration. For instance, the junction,



may be replaced by the following :



in which the potential difference at the junction A may be calculated by means of equation (131) or (132), and that at the junction B by means of equation (129).

92. Flowing junctions.—It has been found that the potential difference at the junction connecting two different salt solutions is variable, and not always reproducible, and most experimenters have tacitly assumed that the highest potential reached, if moderately constant, is the correct value. A method of renewing the interface between the two solutions, so that the potential is constant, is described by Lewis, Brighton and

* *Journ. Amer. Chem. Soc.*, **43**, 2563 (1921).

Sebastian.* Walpole† found that constant potentials could be obtained by forming the junctions with tapes along which the solutions flow. A simple type of flowing junction proposed by Roberts and Fenwick‡ is shown in Fig. 33. M is the type of electrode vessel used for the $\text{Hg}|\text{Hg}_2\text{Cl}_2$ electrode, and S, for the silver-silver chloride electrodes. The lower end of each vessel is bent horizontally, tapered, if necessary, to internal diameter of 2-3 mm., and paraffined near the tip to obviate creeping of the liquid. These tips slide into side tubes in a

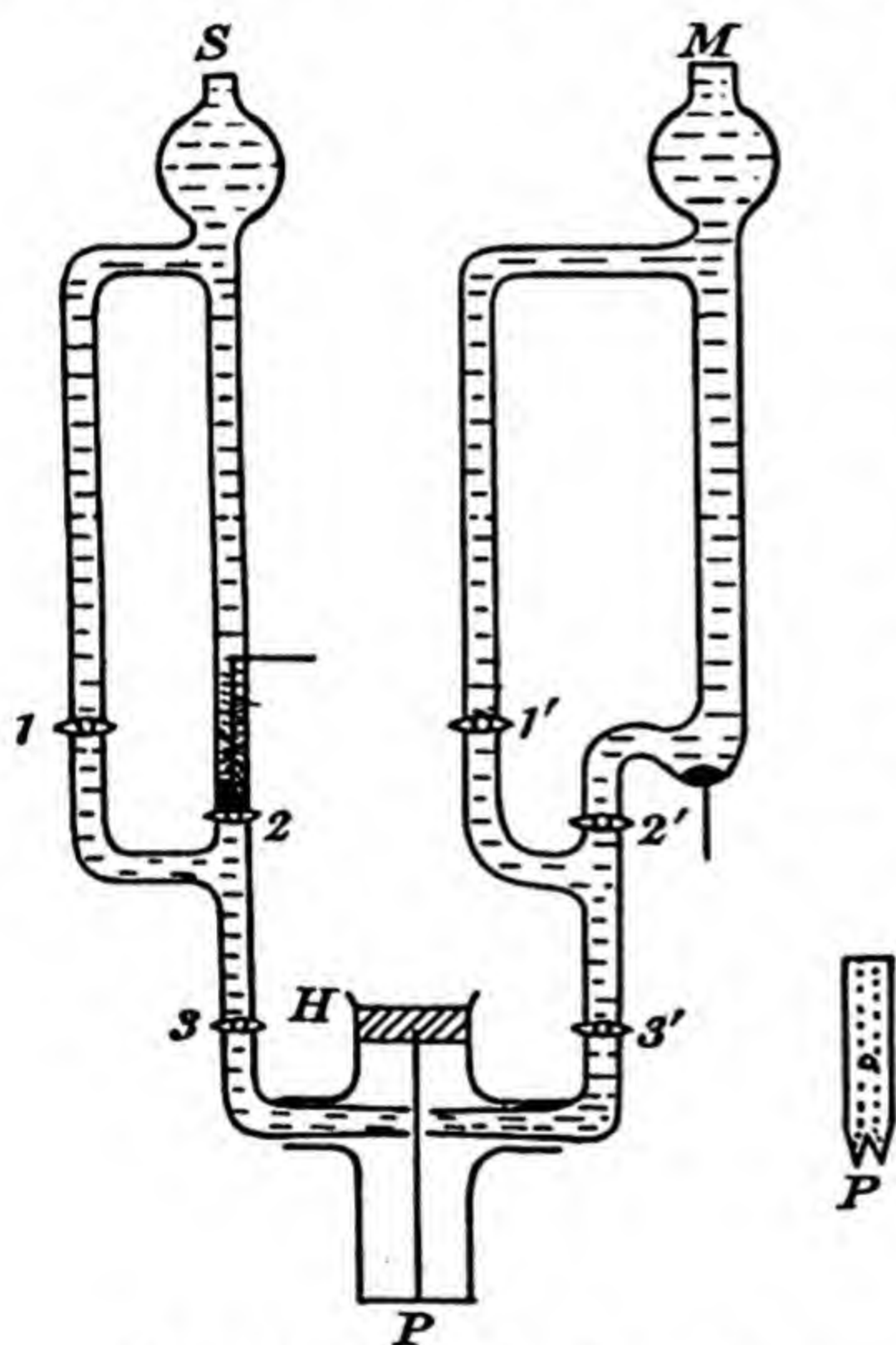


FIG. 33.—A flowing junction.

glass tube H, and are adjusted so that the issuing drops of liquid touch a mica plate P, conveniently held in a rubber stopper. A hole, 1 mm. in diameter, is drilled and placed 5 mm. below the exit tubes of the electrodes. The lower edge of the plate is notched, and the faces painted with hot paraffin wax, except for a narrow channel indicated by dotted lines, past the hole to one of the points, using opposite points on the two sides. This ensures that the only liquid junction is at the aperture in the plate. Taps 3 and 3' are attached to the electrodes for convenience in filling the vessels, while the taps 2 and 2' serve for the washing of the metal electrode.

They are kept closed during actual measurements, the by-pass taps—1 and 1'—being open. Before the mica plate is set in place, the rates of flow of the electrolytes are made equal, as nearly as possible, the rate being 4 to 6 drops per minute. In practice the potential quickly adjusts itself to a constant value. The measured potential differences at the junction of 0.1M HCl and 0.1M KCl, at 25° C., were :

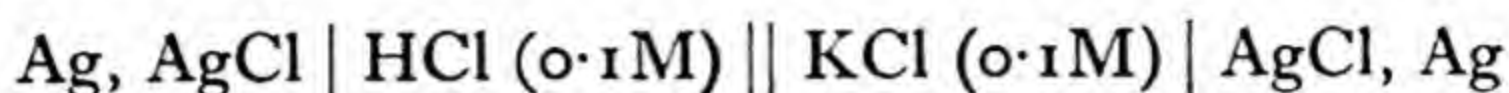
* *Jour. Amer. Chem. Soc.*, **39**, 2245 (1917).

† *Jour. Chem. Soc.*, **105**, 2521 (1914).

‡ *Jour. Amer. Chem. Soc.*, **49**, 2787 (1927).

	millivolts.
Ag, AgCl HCl (0.1M) KCl (0.1M) AgCl, Ag	28.00
Ag, AgCl HCl (0.1M) KCl (0.1M) Hg ₂ Cl ₂ , Hg	73.3
Ag, AgCl KCl (0.1M) Hg ₂ Cl ₂ , Hg	45.30

and, therefore, by difference, the potential difference of the cell



was 28.00 millivolts, which agrees with the value obtained with the first cell.

93. Diffusion potentials.—In a series of papers Prideaux* has shown, experimentally, that definite and reproducible potentials are set up at a parchment paper membrane, which separates two differently concentrated solutions of the same weak organic electrolyte. These potentials resemble the diffusion potentials in the free liquid in many respects, but differ from them numerically. He shows that they can be regarded as modified diffusion potentials, and the transference number for the anion in the membrane, calculated. The membrane potential should probably be regarded as a diffusion potential along the walls of very narrow and tortuous capillaries, through which ions can diffuse. The solution, as a whole, does not flow under moderate pressures.

He calculates the diffusion potential E by means of the equation,

$$E = \frac{u_A - u_K}{u_A + u_K} \cdot \log \frac{\alpha C_1}{\alpha C_2}.$$

Thus for piperidine hydrochloride at 25° C., with $C_1 = 0.1$ and $C_2 = 0.01$ moles per litre, $E = 22.1$ millivolts.

The interposition of a parchment increases the diffusion potential of a salt with a relatively slow anion, and, therefore, it retards the anion more than the kation. On the other hand, the membrane decreases the diffusion potential of a salt having a relatively slow kation, and thus it again retards the anion more than the kation. This is in accordance with the view that the parchment is negative. In the case of acetic acid, the membrane only causes a very slight increase in the diffusion potential. The reason for this may be sought in the diminution of the negative charge on the membrane by the great increase in the hydrogen ion concentration, as compared with its value in the nearly neutral salt solutions. The hydrogen ion might be expected to have a

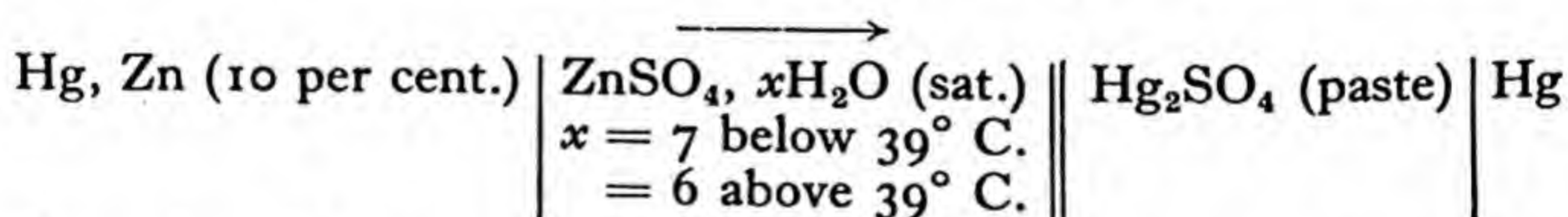
* *Trans. Farad. Soc.*, 10, 160 (1914); 20, 37 (1924); 24, 11 (1928); 25, 20 (1929).

slight discharging effect of this kind, on account of the great increase of its active mass, on either of two hypotheses as to the nature of the surface charge; that is, whether it is due to (a), selective adsorption of anions from the solution, or (b), the binding of anions in an inner, or bound layer, in order to compensate for a slight deficit in the hydrogen ion concentration, caused by preferential adsorption of these ions on the actual wall surface.

The smallness of the effect, observed in the case of weak acids and bases, may be accounted for, by supposing that the mobility of the anion is proportionately reduced in the acids and bases and in their salts. This reduction has a great effect on the difference $u_K - u_A$, or $u_A - u_K$, when these differences are small, as in the case of salts, but only a slight effect on $u_H - u_A$, or $u_{OH} - u_K$, both of which are large.

94. Standard cells.—There are two cells which have been adopted as the practical standard of electromotive force, namely, the Clark cell, and the Weston, or cadmium, cell.

(a) *The Clark cell* consists of zinc amalgam, covered with a layer of zinc sulphate crystals, and pure mercury in contact with a paste of mercurous sulphate, zinc sulphate crystals, and metallic mercury, the electrolyte being a saturated aqueous solution of zinc sulphate and mercurous sulphate. Since the negative electrode, zinc, is in contact with a solution of zinc sulphate, and the positive electrode, mercury, is in contact with mercurous sulphate, the cell is reversible, and may be represented thus:—



If made with pure chemicals, and according to specifications, its electromotive force E_t at a temperature $t^\circ \text{ C.}$, is given by *

$$E_t = E_{15} - 0.00119(t - 15) - 0.000007(t - 15)^2$$

where $E_{15} = 1.4328$ volts.†

(b) *The Weston, or cadmium cell*, has a number of marked advantages compared with the Clark cell. The latter has a fairly high temperature coefficient, it is subject to large hysteresis effects attending temperature variations, its life is comparatively short owing to the tendency of the cell to crack at the point

* Bronson and Shaw, *Electrician*, 66, 698 (1911).

† Ayrton, Mather and Smith, *Phil. Trans.*, A, 207, 463 (1908).

where the platinum terminal is fused into the amalgam limb, and lastly, a layer of gas is formed at the amalgam surface.

The Weston cell is without these disadvantages and has now displaced the Clark cell in the laboratory. The elementary construction of the Weston cell is illustrated in Fig. 34. Pure mercury forms one electrode, and a cadmium amalgam, 10-15 per cent., the other. The mercury electrode is in contact with mercurous sulphate, and the electrolytic solution is one of cadmium sulphate. In one form of cell the cadmium sulphate

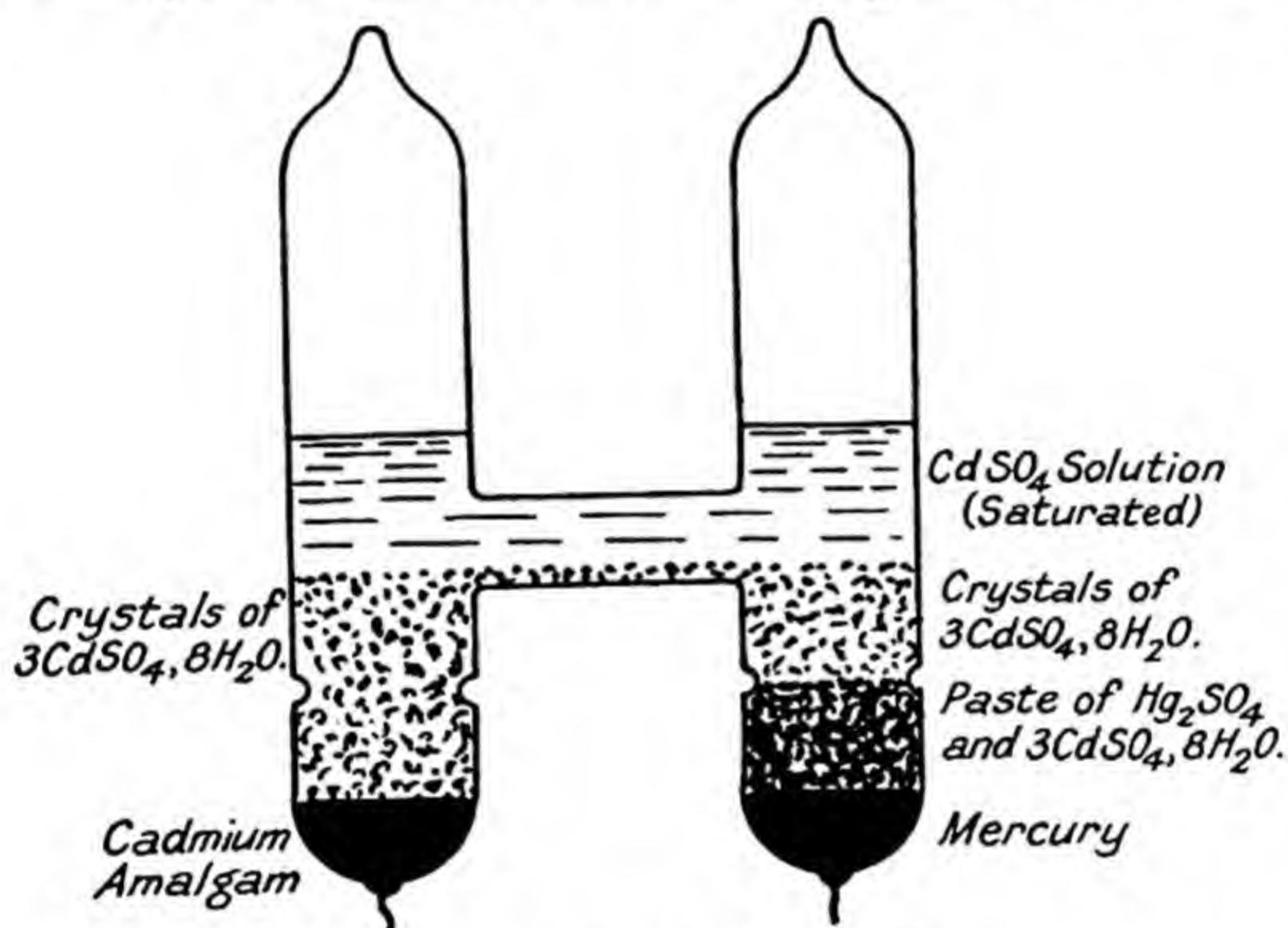
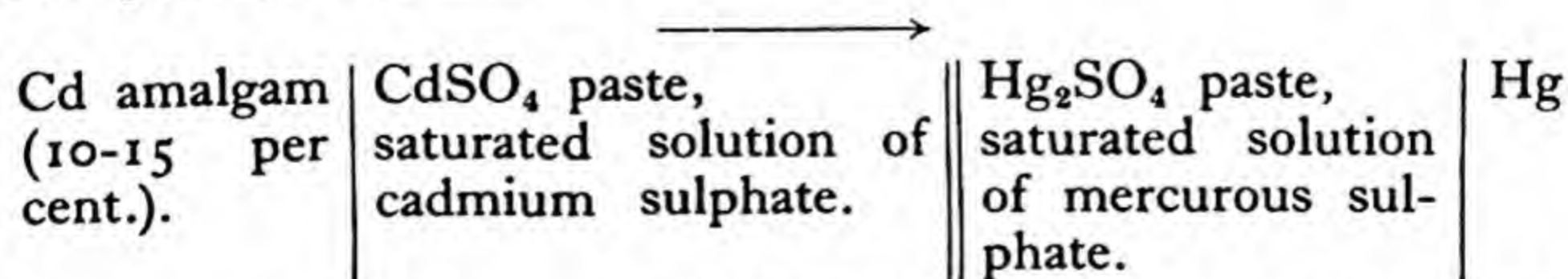


FIG. 34.—The Weston cell.

solution is maintained at the saturation point by placing cadmium sulphate paste in contact with the cadmium amalgam. This type is known as the *saturated*, or *normal*, cell. In another type, the *unsaturated cell*, the concentration of the cadmium sulphate is that of a solution saturated at 4° C. The normal cell may be represented as follows :—



Its electromotive force at 20° C. is 1.01830 volts, and its E.M.F., E_t , at a temperature t° C., is given by *

$$E_t = E_{20} - 0.0000406 (t - 20) - 0.00000095 (t - 20)^2 + 0.00000001 (t - 20)^3.$$

* Adopted by the International Conference in Electrical Units and Standards at London, 1908.

In using standard cells, they should not be exposed to temperatures below 4°C. , or above 40°C. , and current in excess of 0.0001 ampere should never pass through them.

95. Transference numbers from electromotive force measurements.—If we compare equations (118) and (120), we see that for cells containing the same pair of salt solutions, at the same concentrations, the ratio,

$$\frac{\text{E.M.F. of cell with transference}}{\text{E.M.F. of cell without transference}}$$

should be equal to the transference number of one of the ions. By referring to the derivation of the equations it can be seen that in the present case the ratio gives the transference number of the kation. The numbers obtained in this way agree with those measured by other means, as may be seen by comparing the transference numbers for the kation in potassium chloride solutions at 25°C. (See pages 217, 220.)

Concentrations of Solutions.	E.M.F. Ratio.	Transference Numbers.		
		E.M.F. Method.	"Hittorf" Method.	Moving Boundary Method.
0.5N — 0.05N	53.57 : 107.4	.498	.496	—
0.1N — 0.01N	54.00 : 108.9	.496	.496	.493
0.05N — 0.005N	54.70 : 110.85	.494	.496	.493

The general applicability of this method of obtaining transference numbers may be tested by comparing the value it gives for the transference number of the hydrogen ion in hydrochloric acid, with that determined by the "Hittorf" method. Jahn * measured the E.M.F. of the following cells with transference at 18°C. :—

Ag AgCl, HCl	HCl	AgCl Ag	E.M.F. (volt).
" " .003329N	.03330N	" "	.09162 \pm .00005
" " .001665N	.01665N	" "	.09235 \pm .00005

while Tolman and Ferguson † used the following cell without transference at the same temperature :—

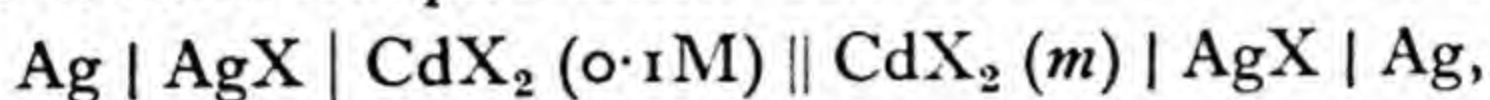
Hg Hg ₂ Cl ₂ , HCl H ₂ — H ₂ HCl, Hg ₂ Cl ₂ Hg	E.M.F. (volt).
" " .002 N 1 atmos. .02N " "	.1109 \pm .001

* *Zeits. phys. Chem.*, **33**, 545 (1900).

† *Jour. Amer. Chem. Soc.*, **34**, 232 (1912).

By means of a linear interpolation from the E.M.F. measurements of the first-mentioned cell, the E.M.F. for concentrations equal to .02 and .002 normal is found to be 0.09210 volt, so that the ratio of the electromotive forces of the two types of cell is 0.830. This number agrees, within the limits of experimental error, with the directly determined transference number, .833, as given by Jahn.*

The concentration cell method of determining the transference numbers is more accurate in the case of uni-univalent electrolytes than the Hittorf method and is now more widely used. For example, Lucasse † has recently obtained some interesting results with concentration cells containing cadmium salts, CdX_2 . As we should expect, the transference number for the kation decreases with concentration, owing to the tendency of these salts to form complex ions. His results for the cell,



were, with cadmium iodide,

Values of m	.01000	.08145	.6908	2.045	4.227	5.133	6.146
Values of n_K	.486	.479	.445	.241	.002	-.104	-.192

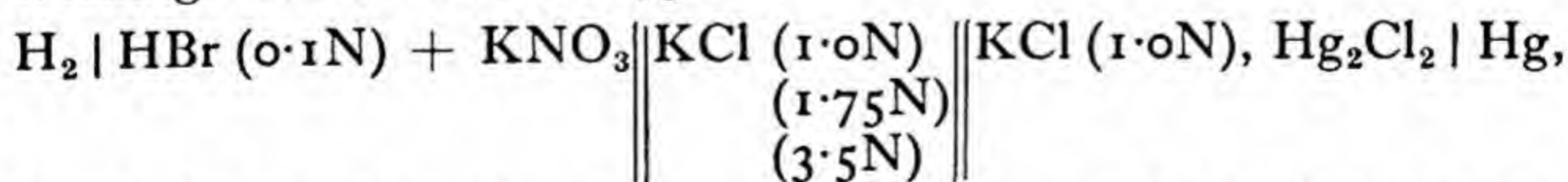
and with cadmium bromide,

Values of m	.01000	.05629	.2026	.8056	1.314	1.896	3.0815
Values of n_K	.434	.424	.371	.115	.015	-.068	-.185

the values of m being expressed in molal units.

96. Concentration cells containing mixed electrolytes.

—The electromotive force of a concentration cell varies when a second electrolyte is present in the main electrolyte. Chow ‡ found with the hydrogen-hydrochloric acid cell containing alkali metal chlorides, that if the total ion concentration was maintained constant, the electromotive force of the cell was given by the usual expression if the value of the total ionic concentration was inserted in the formula. Chow's results have been confirmed by Harned,§ but at high concentrations the electromotive force depends to some extent upon the nature of the added electrolyte. Arkadjev,|| working with cells of the type



found that neutral salts increased the hydrogen electrode potential.

* *Zeits. phys. Chem.*, **37**, 673 (1901).

† *Jour. Amer. Chem. Soc.*, **51**, 2605 (1929).

‡ *Ibid.*, **42**, 497 (1920).

§ *Ibid.*, **42**, 1808 (1920).

|| *Zeits. phys. Chem.*, **104**, 192 (1923).

Concentration of Neutral Salt Moles per Litre.	Measured E.M.F. (Volt).		
	1.0N KCl	1.75N KCl	3.5N KCl
0	.3556	.3539	.3513
0.4	—	.3537	.3517
0.8	—	.3499	.3469
1.2	—	.3456	.3426
1.6	—	.3426	.3402
2.0	.3432	.3393	.3377

Other results * show that the potential of the calcium amalgam electrode is altered when various electrolytes are added to a calcium sulphate solution, but Neuhausen,† investigating the effect of added electrolytes on the reliability of the sodium electrode, concluded that the addition of other electrolytes does not, in general, affect this electrode potential.

97. Amalgam concentration cells.—Another type of concentration cell is one in which the electrodes are composed of the same metal at different concentrations. This may be realised with two differently concentrated amalgams of a single metal. The passage of the metal is from a concentrated to a dilute amalgam, and if we suppose that metals dissolved in mercury exert osmotic pressure like that of ordinary solutions, and that this osmotic pressure is proportional to the metal concentration, C , the electromotive force is given by the familiar relation,

$$E = \frac{RT}{\nu F} \log \frac{C_1}{C_2}, \quad . \quad . \quad . \quad (133)$$

in which C_1 and C_2 denote the respective concentrations of the metal in the amalgams. Pearce and Eversole ‡ have measured the electromotive force existing between various dilute zinc amalgams in contact with a saturated solution of zinc sulphate, and compared the results with those calculated by means of equation (133), assuming that the amalgams behaved as perfect solutions. They found that the observed potentials were less than those calculated from equation (133), and, further, that the deviations from the calculated values increased as the concentration of the zinc in the amalgam was continuously increased. Hulett and Crenshaw § also measured the electromotive force of

* See Fosbinder, *Jour. Amer. Chem. Soc.*, **51**, 1073 (1929).

† *Ibid.*, **44**, 1445 (1922).

‡ *Jour. Phys. Chem.*, **32**, 209 (1928).

§ *Ibid.*, **14**, 175 (1910).

zinc amalgam cells over a concentration range extending from a saturated amalgam to very dilute amalgams. For the range 0.0061 to 0.00000307 normal the electromotive force conformed to the laws of a perfect solution, as indicated by this equation, and it is difficult to explain why these amalgams, when they exceed a certain concentration, suddenly behave as imperfect solutions.

98. Concentration cells with non-aqueous solutions.—

The Nernst formula for the electrode potential of a metal against a solution containing its ions does not explicitly involve any property of the solvent, but there is every reason to suppose that the tendency of the metal ion to go into solution will vary with the nature of the solvent, just as the solubility of any chemical substance varies in different media. The real origin of electrolytic solution tension must, in fact, be sought in the existence of an attractive force between the dipole molecules of the solvent and the ions of the metal. Since the dipole character of the solvent is considered to run parallel to the dielectric constant, and since electrolytes are, in general, more highly ionised in solvents with high than with low dielectric constants, it might be expected that the attraction between the ions and the solvent molecules would increase with the dielectric constant. From this point of view one would expect the solution pressure to increase with increasing dielectric constant. Jones* found that this expectation was realised. He used cells of the type $\text{Ag} | \text{AgNO}_3$ in one solvent $|| \text{AgNO}_3$ in another solvent $| \text{Ag}$. Kahlenberg† also carried out a long series of investigations on the behaviour of ten different metals immersed in solutions of their salts in many different solvents. In one particular case he measured the E.M.F. of cells with silver nitrate in pyridine and in acetonitrile, and compared the results obtained with those calculated from the Nernst equation,

$$E = \frac{RT}{\nu F} \log \frac{A_1 C_1}{A_2 C_2},$$

the liquid-junction potential difference being assumed negligible. Although a fair agreement between the calculated and experimental values had been obtained when aqueous solutions were used, an utter lack of agreement was found with the organic solvents, and he was forced to the conclusion that the formula was not applicable to cells involving non-aqueous solutions. It is known, however,

* *Zeits. phys. Chem.*, 14, 346 (1894).

† *Jour. Phys. Chem.*, 4, 709 (1900).

that complex conditions exist both in solutions of silver nitrate in acetonitrile* and in solutions of this salt in pyridine.† Sakhanov and Grünbaum ‡ verified the Nernst formula with pyridine when the solutions were sufficiently dilute. Koch,§ using silver nitrate in the two solvents, assumed that the ionic concentrations, $[C_1]$, $[C_2]$, could be deduced from the conductance measurements; thus,

$$\frac{[C_1]}{[C_2]} = \frac{\alpha_1 C_1}{\alpha_2 C_2}$$

where

$$\alpha_1 = \frac{\Lambda_1}{\Lambda_0} \text{ and } \alpha_2 = \frac{\Lambda_2}{\Lambda_0}.$$

Putting

$$k_1 = \Lambda_1 C_1 \text{ and } k_2 = \Lambda_2 C_2,$$

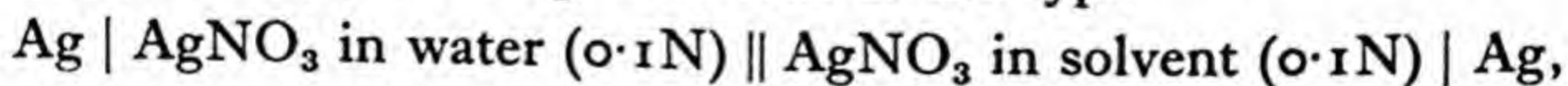
we have from equation (121),

$$E = 2(1 - n_K) \frac{RT}{F} \log \frac{k_1}{k_2}.$$

The results at 0° C. and 25° C. support the Nernst formula, and show that the solution laws are followed in these solvents to the same extent as in water.

Roshdestwensky and McLewis|| worked with cells of silver nitrate in acetone. The two solutions were in direct contact, thus possibly developing a liquid-junction potential difference. Assuming Nernst's law to be valid for these systems, they calculated the transference numbers for the ions, and found that in solutions, varying in concentration between the limits 0.02-0.007 normal, the value for the anion transference number lay between 0.60 and 0.58, and for more dilute solutions it was 0.56.

Henderson,¶ working with cells of the type



obtained the following electromotive forces with different solvents:—

Solvent	ethyl alcohol	methyl alcohol	acetone	aniline	pyridine
E.M.F. (volt)	+0.1004	+0.0967	+0.1712	−0.2559	−0.3618

The values for the transference numbers, calculated from the electromotive force of the cells, are quite different from those

* See Koch, *Jour. Chem. Soc.*, **131**, 647 (1927).

† See Abegg and Neustadt, *Zeits. phys. Chem.*, **69**, 486 (1909).

‡ *J. Russ. Phys. Chem. Soc.*, **48**, 1794 (1916).

§ *Jour. Chem. Soc.*, **132**, 524 (1928).

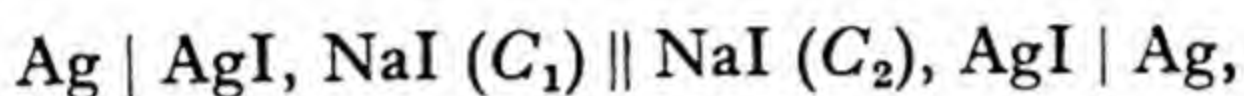
|| *Ibid.*, **101**, 2094 (1912).

¶ *Zeits. phys. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

obtained experimentally. In all cases the experimental values are the greater, but with extremely dilute solutions the calculated values approach more nearly the experimental ones. The anion transfer number increases in value with increasing dilution, except in the case of pyridine, where there is the reverse effect.

Comparing the values of the electromotive force, determined when the aqueous solution is joined to a non-aqueous solution of the same concentration, the solutions in the alcohols and in acetone are positive towards the aqueous solution, but those in aniline and pyridine are negative towards it. The experimental data seem to prove that the abnormalities, observed in non-aqueous solutions of silver nitrate, are due to combination of the solvent and solute to form complex compounds, which dissociate more or less gradually.

Isaacs and Partington* measured the electromotive force of the cells,



using methyl alcohol as the solvent, at 25° C., over concentrations ranging from 0.5 to 0.0001 normal. The values they obtained are given below:—

NaI			KI		
Cell concentrations.	E.M.F. volt.	Anion transference number.	Cell concentrations.	E.M.F. volt.	Anion transference number.
0.1N—0.01N	0.41	.584	0.05N—0.01N	0.0280	.551
0.1N—0.002N	0.72	.583	0.05N—0.002N	0.061	.549
0.01N—0.001N	0.45	.581	0.005N—0.001N	0.0342	.554

Apart from two abnormally high values for the anion transference number, with cells in which the most concentrated solution, 0.5 normal of sodium iodide, was present, all the values of the transference numbers for sodium and potassium in alcoholic solutions, of concentrations from 0.1 to 0.001 normal, were in excellent agreement with those calculated, and were independent of the concentration.

The electromotive force of concentration cells containing a solution of sodium in liquid ammonia has been measured by Kraus† over an extended concentration range. From these measurements approximate values of the transference numbers have been calculated for different concentrations. Assuming that the speed of the positive ion remains constant, the mean speed of the negative ion increases forty-fold within the concentration range

* *Trans. Farad. Soc.*, 25, 53 (1929).

† *Jour. Amer. Chem. Soc.*, 36, 864 (1914).

0.001-1.0 normal, and if the equivalent conductance of the positive ion is assumed to be 130, the equivalent conductance of the dilute metal solution is calculated to be 1040. These curious results are accounted for on the assumption that both Na^+ ions and electrons exist in solution. At high dilutions the electrons, which serve as negative ions, are surrounded by envelopes of ammonia, and the size of these envelopes determines the speed of the negative ions.

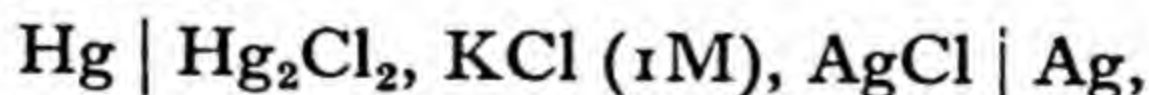
99. Temperature coefficient of concentration cells.—Equation (107),

$$E = -\frac{H_v}{\nu F} + T \frac{\partial E}{\partial T},$$

expressing the relation between the electromotive force of a cell and its temperature coefficient, $\frac{\partial E}{\partial T}$, is applicable to all types of reversible cells, and since for concentration cells there is no heat of reaction, $H_v = 0$, and therefore

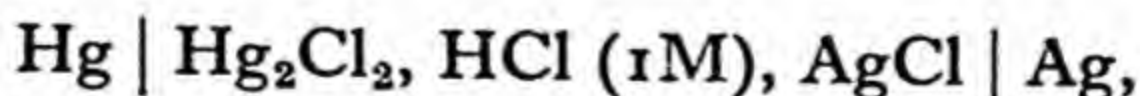
$$E = T \frac{\partial E}{\partial T},$$

or, the electromotive force is proportional to the absolute temperature. This is only true when the substances are so dilute that no appreciable amount of heat is evolved on further dilution, and $\frac{\partial E}{\partial T}$ is positive. Gerke* measured the electromotive force of various cells at different temperatures. His measurements include the following:—



E.M.F. observed.	Temperature.	Temperature Coefficient.
0.04551 volt.	24.86° C.	+ 0.00336 volt per 1° C.
0.04215 „	14.86° C.	

and



E.M.F. observed.	Temperature.	Temperature Coefficient.
0.04544 volt.	24.86° C.	+ 0.00338 volt per 1° C.
0.04206 „	14.86° C.	

100. Gas cells.—Another type of concentration cell in which the electrodes are of different concentrations is the gas cell. For example, if we have two well platinised-platinum electrodes in contact with hydrogen gas, the pressure of the gas

* *Jour. Amer. Chem. Soc.*, 44, 1684 (1922).

being different at the electrodes, and if they are immersed in an acid or an alkali solution, an electric current will flow when the two electrodes are joined, gas dissolving at the electrode of high pressure and appearing at that of low pressure. If the gas pressures are p_1 and p_2 , respectively, and $[C_1]$ and $[C_2]$ are the hydrogen ion concentrations in the immediate neighbourhood of the two electrodes, respectively, we may imagine a thermodynamic cycle at constant temperature to be performed on the system by allowing an electric current to flow reversibly against a balancing electromotive force, taking out the gas evolved, slowly compressing it, and then transferring it to the other compartment. The original state of the system is then restored. Further, we may assume that the ideal gas laws are obeyed, and that the hydrogen can pass from the gas phase on the one side to yield hydrogen ions, and, *vice versa*, at the other electrode. No work is done in converting the gas from a pressure p_1 to the ionic state at concentration $[C_1]$. If one faraday, F , of electricity passes, osmotic work equal to

$$RT \log \frac{[C_1]}{[C_2]}$$

is done by the system in transferring 1 gram-equivalent of hydrogen ions from the concentration $[C_1]$ to that of $[C_2]$. No work is required to pass from this latter state to the gas state at pressure p_2 , but work equal to *

$$\frac{RT}{2} \log \frac{p_1}{p_2}$$

must be done on the system to restore the gas from the pressure p_2 to its original state p_1 . The electrical energy lost by the system is EF , where E is the electromotive force of the cell. Thus,

$$EF = RT \log \frac{[C_1]}{[C_2]} - \frac{RT}{2} \log \frac{p_1}{p_2},$$

i.e.,
$$E = \frac{RT}{F} \log \frac{[C_1]}{[C_2]} - \frac{RT}{2F} \log \frac{p_1}{p_2},$$

or
$$E = \frac{RT}{F} \log \frac{[C_1] \sqrt{p_2}}{[C_2] \sqrt{p_1}}. \quad (134)$$

If the hydrogen ion concentrations are equal,

$$E = \frac{RT}{2F} \log \frac{p_2}{p_1}, \quad (135)$$

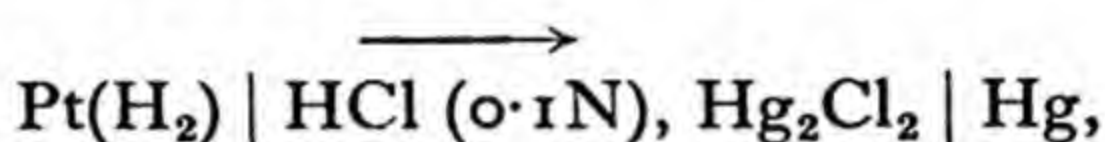
* The factor $\frac{1}{2}$ is introduced since two hydrogen ions pass from the ionic state to form one molecule of gas.

and if the pressure of the gas at the two electrodes is the same, and is maintained so while the electromotive force is being measured, then,

$$E = \frac{RT}{F} \log \frac{[C_1]}{[C_2]}. \quad (136)$$

The pressures may be kept constant by allowing the gas to bubble slowly through the vessels containing the electrodes while the measurements are being made. Since a *decrease* in the gas pressure corresponds to a *decrease* in the electrolytic solution pressure of hydrogen, it will be noted that the electrode in contact with the gas at the *lower* pressure is *positive* with respect to the other electrode.

Although this hydrogen cell is never used in practice, the hydrogen electrode forms a convenient standard electrode, and is used as such in conjunction with other electrodes in various concentration cells. For example, if it is combined with a mercurous chloride electrode, the *calomel electrode*, the variation of the hydrogen electrode potential with gas pressure may be investigated. Thus, Hainsworth and MacInnes* measured the electromotive force of the cell,



at 25° C. for various hydrogen gas pressures up to 400 atmospheres. If δE is the change in the E.M.F. of this cell, produced by changing the pressure from one atmosphere to p atmospheres, then, from equation (135),

$$\delta E = \frac{RT}{2F} \log p.$$

Their results were as follows :—

Pressure in Atmospheres (p).	δE (Observed).	δE (Calculated).
50	0.0504 volt.	0.0506 volt.
100	0.0594 "	0.0598 "
200	0.0688 "	0.0694 "
300	0.0745 "	0.0753 "
400	0.0787 "	0.0797 "

Another type of gas cell is the chlorine—silver chloride—silver cell,† shown in Fig. 35.

101. Oxidation-reduction cells.—Another process which supplies electrical energy is that of oxidation, or reduction, during which the valency of the ions taking part in the process

* *Jour. Amer. Chem. Soc.*, **44**, 1021 (1922).

† See Gerke, *ibid.*, **44**, 1690 (1922).

is changed. In *oxidation processes* charges of *positive* electricity are added to, or *negative* charges are *withdrawn from*, the atoms, ions or molecules, whereas in *reduction* processes the converse takes place. A divalent ferrous ion, on taking up a third unit of positive electrical charge, is oxidised, becoming a trivalent ferric ion. On the other hand, a trivalent ferric ion may be reduced to a divalent ferrous ion. There is a simple relationship between the quantity of electricity gained, or lost, and the weight of the substance affected, a change in the charge of 96,491 coulombs, corresponding to the gain, or loss, of one formula weight in grams

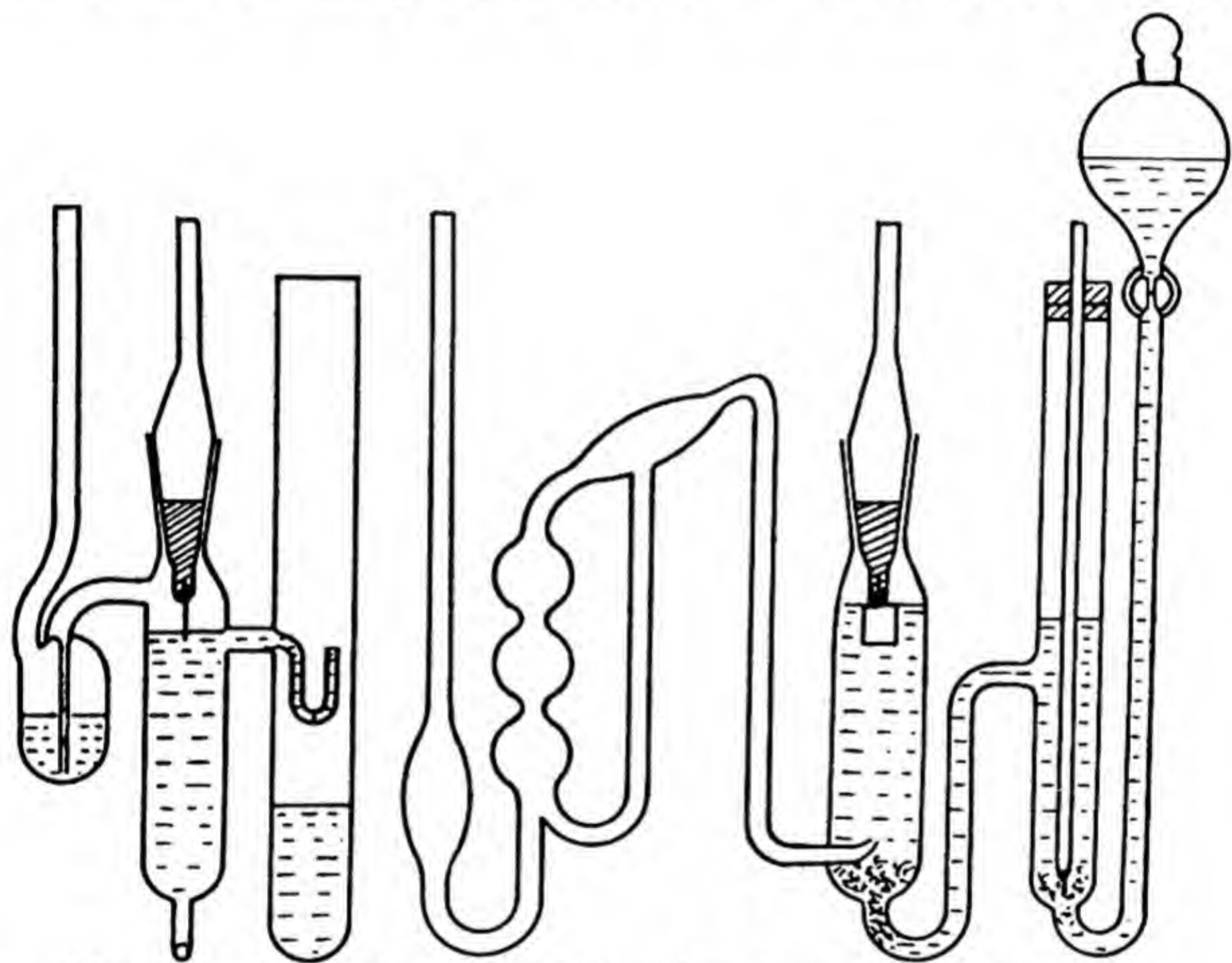
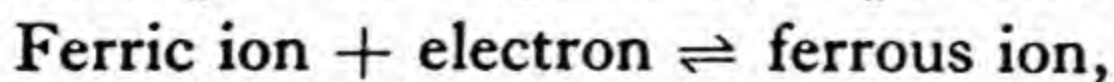


FIG. 35.—A chlorine—silver chloride—silver concentration cell.

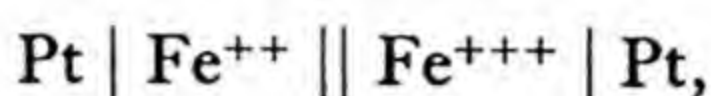
of the substance involved. In every oxidation-reduction process the charge which is lost by the one reacting substance must of necessity be gained by the other.

So far we have considered the oxidation-reduction processes to depend upon the loss, or gain, of positive electrical charges, but they might just as easily be considered in terms of the changes of negative electrical charges. Indeed, it is now generally agreed that one of the fundamental parts of the process is an exchange of electrons. Thus, in the case of a ferric-ferrous system the oxidation-reduction process is generally represented by



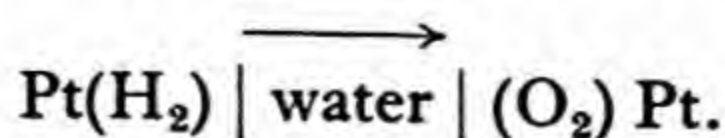
where ϵ represents an electron. This reversible process is not dependent upon the presence of any electrode, the exchange of electrons taking place continuously. We may look upon the electrons as exerting a pressure, similar in character to the solution pressure of metals, postulated by Nernst.

Let us consider a platinum electrode to be placed in an acid solution of ferrous and ferric chlorides. The electrode almost immediately assumes a stable potential, the value of which is determined by the ratio of the number of ferrous to ferric ions. We may therefore form a cell such as



where the two solutions containing the iron ions are connected by means of an inactive intermediate solution. If the platinum electrodes are joined by a wire, a *positive* current passes along the *wire* from the right-hand electrode to the other. The ferrous ions each give up one electron to the electrode on the left, and become converted into ferric ions. We can imagine that these electrons, thus liberated, then travel along the wire and pass into the cell at the other electrode, converting the ferric ions into ferrous ions. This electric current would continue, if allowed to do so, until the relative concentrations of the two sets of ions in the two solutions become equal. This arrangement is known as an *oxidation-reduction* cell.

Gas cells may also be considered as oxidation-reduction cells. If we apply a potential difference of about 2 volts between platinum plates, immersed in dilute sulphuric acid, oxygen and hydrogen gases collect at the respective plates, and the latter, which are neutral to begin with, are transformed into oxygen and hydrogen electrodes, respectively, the former being positive with respect to the latter. Theoretically, only water is necessary for the process, but acid is added to increase the conductivity of the liquid. If the decomposing current is stopped, and the cell examined, it is found to possess an electromotive force of 1.1 volts, approximately. If an electric current is taken from the cell, the hydrogen gas ionises at the hydrogen electrode and passes across to the oxygen electrode, while at the other electrode the oxygen ionises and unites with the water to form hydroxyl ions, thus,



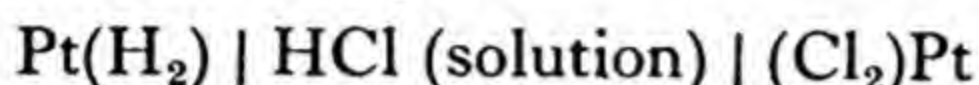
The theoretical value of the electromotive force of this cell may be calculated from equation (107), since two moles of

water are formed when four faradays of electrical charge pass. Neglecting $\frac{\partial E}{\partial T}$ we have

$$E = -\frac{2H_v}{4F} \text{ approximately.}$$

The calculated value is 1.23 volts which is higher than that experimentally determined. Some platinum oxide may be formed during the process, and this substance has a potential different from that of pure oxygen.

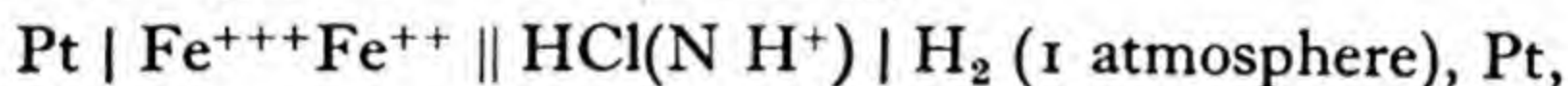
In a similar manner the system



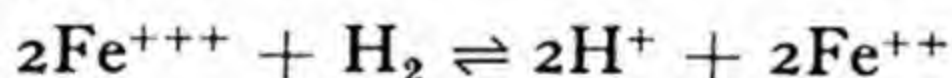
forms an oxidation-reduction cell, the electromotive force of which has been measured by Müller.* His values at different acid concentrations were,

Concentration of acid	1.0N	0.1N	0.01N	0.001N
E.M.F. at 25° C.	1.3660	1.485	1.546	1.587 (volts)

102. Oxidation potential.—The potential assumed by an inactive electrode, such as platinum, when immersed in an oxidation-reduction system, may be compared with that of a standard electrode. Thus, suppose we form a cell, using the normal hydrogen electrode, of the type



in which the reaction



occurs, the direction of the reaction depending upon the relative concentrations of the ferric and ferrous ions. If oxidation of the ferrous ions takes place the positive current passes through the cell from left to right, and in the opposite direction if reduction occurs. For the latter process, when equilibrium is attained, the equilibrium constant, K , of the reaction is given by (equation 29),

$$K = \frac{[\text{Fe}^{++}]_0^2 [\text{H}^+]_0^2}{[\text{Fe}^{+++}]_0^2 [\text{H}_2]_0},$$

the suffix $_0$ denoting the concentration of the various reactants and resultants at the equilibrium state. The free energy change, $\delta\psi$, per mole of hydrogen, in this process is, from equation (31),

$$\delta\psi = -RT \log K + RT \log \frac{[\text{Fe}^{++}]^2 [\text{H}^+]^2}{[\text{Fe}^{+++}]^2 [\text{H}_2]}.$$

* *Zeits. phys. Chem.*, 40, 158 (1902).

But this free energy change is also given by

$$-\delta\psi = 2F\mathbf{E}$$

where \mathbf{E} is the electromotive force of the cell. Hence, since the concentrations of the hydrogen ions and the hydrogen gas are constant, we may write,

$$\mathbf{E} = \frac{RT}{2F} \left[\log K' - \log \frac{[\text{Fe}^{++}]^2}{[\text{Fe}^{+++}]^2} \right],$$

where
$$K' = \frac{[\text{Fe}^{++}]_0^2}{[\text{Fe}^{+++}]_0^2}.$$

Putting $\frac{RT}{2F} \log K' = \mathbf{E}_0$, we obtain

$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{F} \log \frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}. \quad (137)$$

R , T and F have their customary significances, and $[\text{Fe}^{++}]$ and $[\text{Fe}^{+++}]$ represent concentrations of the ferrous and the ferric ions, respectively. Since one half of the cell is the normal hydrogen electrode, \mathbf{E} is the potential, referred to the hydrogen scale, of the electrode in the oxidation-reduction system. If the concentrations of the ferric and the ferrous ions are identical, then $\mathbf{E} = \mathbf{E}_0$, where \mathbf{E}_0 is termed the *normal reduction potential* of the process. It is a constant characteristic of this particular oxidation-reduction process. \mathbf{E} is known as the *reduction potential* of the electrode $\text{Pt} | \text{Fe}^{++}, \text{Fe}^{+++}$.

Equation (137) is sometimes written thus :

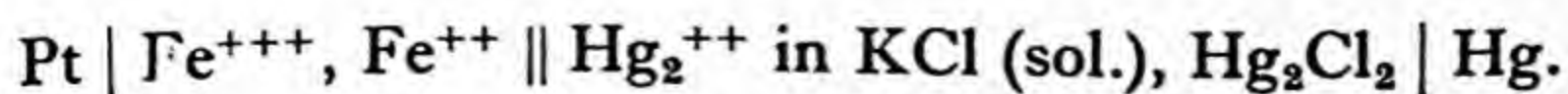
$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{F} \log \frac{[\text{Red}]}{[\text{Ox}]},$$

where $[\text{Red}]$ is the concentration of the *reductant* agent and $[\text{Ox}]$ that of the *oxidant*.

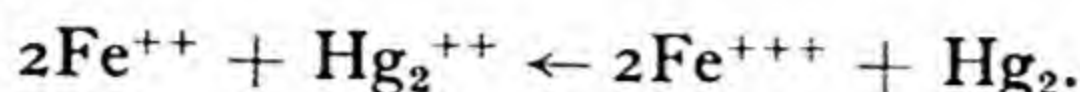
In a similar manner, the oxidation potential in the above cell may be obtained by writing $K_1 = \frac{1}{K}$, where

$$K_1 = \frac{[\text{Fe}^{+++}]_0^2 [\text{H}_2]_0}{[\text{Fe}^{++}]_0^2 [\text{H}^+]_0^2}.$$

Instead of using the hydrogen electrode, the calomel electrode may be substituted for it, thus,



Taking the reaction occurring within the cell as being represented by the equation,



The equilibrium constant K is given by

$$K = \frac{[\text{Fe}^{++}]_0^2 [\text{Hg}_2^{++}]_0}{[\text{Fe}^{+++}]_0^2 [\text{Hg}_2]_0}.$$

Since the concentrations of the mercury and the mercurous ions are constant, we have, as before,

$$K' = \frac{[\text{Fe}^{++}]_0^2}{[\text{Fe}^{+++}]_0^2},$$

and
$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{F} \log \frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}.$$

In general, we may write,

$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{\nu F} \log \frac{[C_1]}{[C_2]}, \quad (138)$$

where $[C_1]$ and $[C_2]$ are the ionic concentrations of the lower and higher degrees of oxidation, respectively, in a cell in which reduction of the ions takes place, \mathbf{E}_0 is the electromotive force of the cell when $[C_1] = [C_2]$, and ν represents the difference in the total valence of the species taking part in the oxidation.

The exact nature of the process occurring during oxidation, or reduction, at an inert electrode is not known, and different theories have been suggested, but they are not entirely satisfactory. One such theory has been formulated by Butler.* He supposes that when an inert electrode is dipped into a solution containing two substances, related by a simple oxidation-reduction process, the ions in the immediate vicinity of the surface must come into contact with it from time to time, and if there is any affinity between the metal surface and the ions, they may be adsorbed to some extent. The electrodes which give the best defined potentials are those whose surfaces possess good adsorptive properties, such as platinised platinum. If the surface does not exert any specific attraction on the solute molecules, those which come into contact with the surface are not held, and can pass again into solution without performing any work against the surface attractive forces. If the surface does exert a specific attraction on the solute molecules, those which reach the surface cannot escape until they have acquired sufficient kinetic energy to overcome the

* *Trans. Farad. Soc.*, 19, 734 (1924).

surface attractive forces. Butler determines the oxidation potential in terms of the ionisation potential, corresponding to the loss of an electron by the reduced molecule, the difference in the energies of hydration of the two substances concerned, the affinity of the metal and statistical constants.

103. Measurement of oxidation potential.—The oxidation potential is measured experimentally by placing the two oxidation-reduction systems in liquid junction with an intermediate solution, which is not attacked chemically by either oxidation-reduction component. This solution eliminates any liquid junction potential, produced by unequal rates of diffusion, and keeps the two oxidation-reduction systems from interacting. The measurement of the electromotive force of such a system obviously gives the difference between the oxidation potentials of the two systems. The system $\text{Pt}(\text{H}_2) | \text{H}^+$ is the important reducing system, having a great tendency to give up electrons so that the electrode is charged negatively, and it is convenient to measure the potential of all oxidation-reduction processes against that occurring at the hydrogen electrode. Even if the latter cannot be combined with a particular oxidation process to form a cell, the electrode potential may be expressed relatively to that of the normal hydrogen electrode—taken as zero. Having obtained the value of E (equation 138), relative to the normal hydrogen

TABLE LVI.
OXIDATION POTENTIALS.

Solution.	E (Volts).	Solution.	E (Volts).
Stannous chloride, potassium hydroxide	− 0.578	Sulphurous acid	+ 0.442
Hydroxylamine, potassium hydroxide	− 0.333	Ferrous sulphate, sulphuric acid	+ 0.517
Pyrogallal acid, potassium hydroxide	− 0.196	Iodine, potassium iodide	+ 0.612
Hydroquinone, potassium hydroxide	− 0.043	Potassium ferricyanide	+ 0.707
Potassium ferro-oxalate	+ 0.013	Potassium bichromate	+ 0.788
Potassium ferrocyanide	+ 0.198	Chlorine, potassium hydroxide	+ 0.908
Iodine, potassium hydroxide	+ 0.213	Ferric chloride	+ 0.961
Stannous chloride, hydrochloric acid	+ 0.220	Nitric acid	+ 0.979
Sodium hypophosphite	+ 0.241	Bromine, potassium hydrate	+ 1.145
Cuprous chloride	+ 0.283	Potassium iodate, sulphuric acid	+ 1.220
Sodium sulphite	+ 0.308	Manganese dioxide, hydrochloric acid	+ 1.353
Sodium hypophosphate	+ 0.318	Chlorine, potassium chloride	+ 1.391
Ferrous sulphate (neutral)	+ 0.356	Potassium permanganate, sulphuric acid	+ 1.483

electrode, the value of the normal oxidation-reduction potential, E_0 , may be calculated from this equation. Bancroft* carried out several experiments on the oxidation potentials by immersing platinum electrodes in solutions, taking potassium permanganate in sulphuric acid as the most energetic oxidising agent. Most of his solutions contained 0.2 moles of electrolyte per litre. His results, referred to the normal hydrogen scale, are given in Table LVI.

TABLE LVII.

NORMAL OXIDATION-REDUCTION POTENTIALS.

Reaction.	E_0 (Volts).	Reaction.	E_0 (Volts).
1. $\text{Co}^{+++} + \epsilon = \text{Co}^{++}$	1.817	6. $\text{Cu}^{++} + \epsilon = \text{Cu}^+$	0.448
2. $\text{Ce}^{++++} + \epsilon = \text{Ce}^{+++}$	1.55	7. $\text{Sn}^{++++} + 2\epsilon = \text{Sn}^{++}$	0.440
3. $\text{Tl}^{+++} + 2\epsilon = \text{Tl}^+$	1.211	8. $\text{Ti}^{++++} + \epsilon = \text{Ti}^{+++}$	0.336
4. $\frac{1}{2}\text{Hg}_2^{++} + \epsilon = \text{Hg}^+$	0.901	9. $\text{V}^{+++} + \epsilon = \text{V}^{++}$	0.148
5. $\text{Fe}^{+++} + \epsilon = \text{Fe}^{++}$	0.747		

1. Lamb and Larson, *Jour. Amer. Chem. Soc.*, **42**, 2024 (1920).
2. Baur and Glaessner, *Zeits. Elektroc.*, **9**, 534 (1903).
3. Grube and Hermann, *ibid.*, **26**, 291 (1920).
4. Popoff, Dissertation.
5. Popoff and Kunz, *Jour. Amer. Chem. Soc.*, **51**, 382 (1929).
6. Bodlander and Störbeck, *Zeits. anorg. Chem.*, **31**, 465 (1902).
7. Foerster and Yamasaki, *Zeits. Elektroc.*, **17**, 361 (1911).
8. Diethelm and Foerster, *Zeits. phys. Chem.*, **62**, 138 (1908).
9. Rutter, *Zeits. anorg. Chem.*, **52**, 368 (1907).

Values of the normal oxidation potential, E_0 , at 25° C., are given in Table LVII. In all cases the reaction tends to take place from left to right as written when opposed to a normal hydrogen electrode, and $\frac{1}{2}\text{H}_2 = \text{H}^+ + \epsilon$ is taken to be zero potential.

104. Applications of concentration cells.—From what has been said previously, if two electrodes of the same metal are placed in solutions containing the ions of the metal at different concentrations, $[C_1]$ and $[C_2]$, respectively, and these solutions are placed in electrical contact, either through a porous partition, or by means of a siphon, or even separated by gravity alone, there exists between the two electrodes a potential difference, E , expressed, approximately, by means of the formula

$$E = 0.000198 \frac{T}{\nu} \log_{10} \frac{[C_1]}{[C_2]},$$

* *Zeits. phys. Chem.*, **10**, 387 (1892).

where ν is the valence of the metal ions in solution and T the absolute temperature.

$$\text{At } 18^\circ \text{ C.,} \quad E = \frac{0.058}{\nu} \log_{10} \frac{[C_1]}{[C_2]},$$

so that if $[C_1]$ is known, it is possible to determine, quite accurately, even very small ionic concentrations. The same principle can be applied to the determination of the hydrogen ion concentration in acids, or alkalis, if, for electrodes, we use a noble metal like platinum, saturated with hydrogen under a definite pressure. If we use such an electrode, dipping into a solution containing normal concentration of hydrogen ions, *i.e.*, $[H_1^+] = 1$, and measure the potential difference between it and another similar electrode, which is immersed in a solution of which the hydrogen ion concentration $[H^+]$ is unknown, the two solutions being connected by a siphon containing concentrated potassium nitrate, or potassium chloride solution, then, the unknown concentration and the potential difference are related according to the expression

$$E = 0.058 \log_{10} \frac{1}{[H^+]}$$

In practice it is more convenient to combine the solution, containing the hydrogen ions of unknown concentration, with the standard calomel electrode, and measure the electromotive force of the resulting cell. If E_c is the value thus obtained, then, as shown in **section (85)**, at 25° C. ,

$$E_c = 0.059 \log_{10} \frac{1}{[H^+]} + 0.282.$$

Since the values of $[H^+]$ vary tremendously in different solutions, it is convenient to make use of the function $\log_{10} \frac{1}{[H^+]}$, instead of values of $[H^+]$. This function is denoted by the symbol pH . Hence,

$$pH = -\log_{10} [H^+].$$

If, for example, pH is equal to 7, $[H^+]$ has the value 10^{-7} . It will be observed that pH decreases as $[H^+]$ increases, *i.e.*, as the acidity of the solution increases. Values of pH may, therefore, be determined by immersing a platinum electrode in the solution, combining this half-cell with a normal calomel electrode, or the normal hydrogen electrode, and measuring the electromotive force of the resultant cell.

In the case of water we have

$$[\text{H}^+][\text{OH}^-] = K, \text{ approximately,}$$

where $[\text{H}^+]$ and $[\text{OH}^-]$ are the ionic concentrations of the hydrogen and the hydroxyl ions, respectively, and K is the equilibrium constant of water, or more strictly, the ionic product. Therefore, in all aqueous solutions, whether strongly alkaline or acid, there must be sufficient hydrogen or hydroxyl ions, respectively, to maintain a constant value of this ionic product. When the concentrations of the hydrogen and the hydroxyl ions in a solution are equal, the solution is neutral, and hence, since $K = 10^{-14}$, approximately, a solution is neutral if

$$[\text{H}^+]^2 = [\text{OH}^-]^2 = 10^{-14},$$

or $[\text{H}^+] = 10^{-7}$, *i.e.*, $\text{pH} = 7$. In other words, the pH value 7 is a convenient reference point with which to differentiate "acid" from "alkaline" solutions.

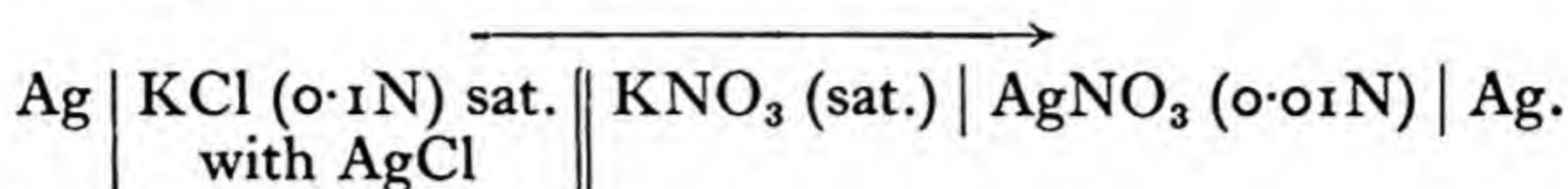
This result provides a rapid and accurate method of determining the *neutralisation point* of an acid, or an alkali, the hydrogen electrode taking the place of an *indicator* in the process. In using this *electrometric titration* method, a hydrogen electrode is placed in the acid solution, and the latter is connected with a normal calomel electrode to form a cell. If an alkali is now carefully titrated into the acid solution, neutrality will be attained when the pH value of the solution is equal to 7, and at this point the electromotive force of the cell, at 25°C ., will be E_c , where

$$E_c = 0.059 \log_{10} \frac{1}{10^{-7}} + 0.282 = 0.695 \text{ volt.}$$

The cell forms one branch of a potentiometer arrangement, the electromotive force of the cell being measured after each small addition of the alkali. When the E.M.F. reaches the value 0.695 volt, the solution is neutral. Since it is difficult to titrate the exact amount of alkali necessary to attain neutralisation, it is more usual to plot values of the E.M.F. against the volume of alkali added. The resulting curve shows a rapid change of E.M.F. with the amount of added alkali at the neutral point, and the latter can thus be determined from the curve.

The solubility of sparingly soluble salts in solvents may also be determined from the measured electromotive forces of concentration cells, and this method is available when others are inapplicable.

Let us consider the cell



We have from equation (88),

$$[\text{Ag}^+][\text{Cl}^-] = s_0,$$

where s_0 is the solubility product, s , the solubility, being given by $\sqrt{s_0}$. Actually in the KCl (0.1N), AgCl solution the concentration of the chloride ions is 0.1 normal, approximately, so that s is equal to $\sqrt{[\text{Ag}^+]0.1}$, where $[\text{Ag}^+]$ is the number of gram equivalents per litre of the silver ions in this solution. If E is the measured E.M.F. of this cell, then,

$$E = 0.058 \log_{10} \frac{0.01}{[\text{Ag}^+]},$$

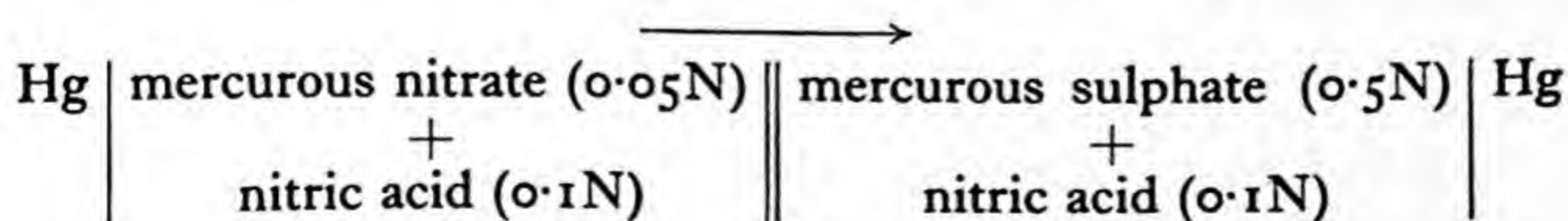
and thus $[\text{Ag}^+]$ may be calculated and s and s_0 determined. The solubility products and solubilities, at 25° C., of various salts in methyl alcohol, and in water, determined in this way, are given in Table LVIII.*

TABLE LVIII.

SOLUBILITY PRODUCTS AND SOLUBILITY IN WATER AND IN METHYL ALCOHOL.

Salt.	Solubility Product in Methyl Alcohol.	Solubility in Methyl Alcohol (Gram-Equivalents per 1000 Grams).	Solubility in Water (Gram-Equivalents per 1000 Grams).	Solubility in Water. Solubility in Methyl Alcohol
AgCl	8.9×10^{-14}	3.0×10^{-7}	1.3×10^{-5}	43
AgBr	5.9×10^{-16}	2.4×10^{-8}	7.8×10^{-7}	33
AgI	6.0×10^{-19}	7.7×10^{-10}	1.0×10^{-8}	13
AgCNS	1.3×10^{-14}	1.3×10^{-7}	1.2×10^{-6}	9.2
TlCl	2.9×10^{-5}	5.4×10^{-3}	1.5×10^{-2}	2.8

The valency of an ion in a concentration cell may be determined from electromotive force measurements. By this means Ogg † found the valency of mercurous ions in the cell,



* See Buckley and Hartley, *Phil. Mag.*, 8, 320 (1929).

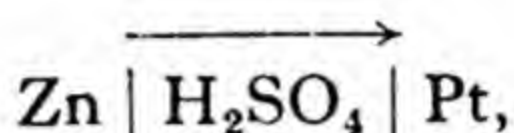
† *Zeits. phys. Chem.*, 27, 285 (1898).

Taking the concentration of the mercurous ions as proportional to the salt concentration, the E.M.F. of this cell, E , is given by

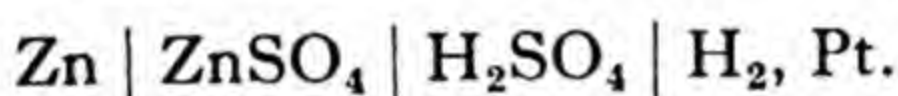
$$E = \frac{RT}{\nu F} \log \frac{0.5}{0.05} = \frac{0.058}{\nu} \log_{10} 10.$$

Actually the E.M.F. of the cell, at 18°C. , is 0.029 volt, and thus the mercury ions are divalent.

105. Irreversible cells.—Some of the cells in common use are essentially irreversible in action, as, for example, the simple type,



which gives rise to a current of which the value soon falls to practically zero, since hydrogen collects at the platinum electrode and produces polarisation effects which will be more fully discussed in Chapter VIII. The cell becomes, in principle,



The hydrogen possesses a greater solution pressure than the platinum, and as this solution pressure is proportional to the pressure of the gas evolved, we may imagine it to reach a value equal to that of the zinc, when the current ceases. The smaller the solution pressure of the gas, the higher is the electromotive force of the cell, but it is evident that this electromotive force will not remain constant unless the hydrogen is removed as quickly as it is evolved. In practice this is not possible in the absence of oxidising agents.

106. Photo-voltaic cells.—Becquerel* found that when two metallic electrodes were coated with a photo-sensitive material, and were immersed in an electrolyte, if one of these electrodes was illuminated while the other was kept in the dark, an electromotive force was set up. He observed that with silver-silver iodide electrodes, this *photo-potential* was not always in the same direction. If the silver iodide coating on the electrode was not too thick, light focussed on the electrode caused the latter to take a positive charge from the liquid, but after the coating had reached a critical thickness there appeared a negative effect, which was only temporary, however, and was ordinarily followed by a positive effect. Becquerel used his silver-silver halide electrodes in a solution containing a small amount of sulphuric acid. Solutions of eosin, fluorescein, *etc.*, also show the effect.

* *La Lumière*, II., 129 (1868).

Scholl,* Goldmann,† Wildermann,‡ Garrison§ and many others have investigated these cells. Tucker|| set forth the following group of generalisations as a basis for explaining and predicting the behaviour of a given voltaic cell.

(a) In a photo-voltaic cell with electrodes consisting of the same material from which the metallic constituent of the photo-sensitive material is derived, illumination tends to produce a photo-chemical reduction of the photo-sensitive substance.

(b) If the photo-sensitive substance is on the illuminated electrode as a uniform layer, local cell formation on the illuminated surface will be at a minimum, and the exposed electrode will be an anode.

(c) If the photo-sensitive substance is on the illuminated electrode as a non-uniform layer, local cells will be set up within it, and if these local cells tend to polarise, the illuminated electrode will eventually become a kathode after continued illumination. If, on the other hand, these local cells do not polarise, but are perfectly reversible, the electrical behaviour of the illuminated electrode will be determined by the oxidising, or reducing, nature of the cell solution. In an oxidising solution, or a neutral solution, the illuminated electrode will be a kathode, while in a reducing solution it will be an anode.

Murdock¶ worked with films of platinum on glass, and a 6 per cent. solution of rhodamine B in absolute alcohol. He found that the density of the current, after a time t , following an exposure of one minute, or less, is well represented by the equation,

$$y = y_0 - \frac{t}{Mt + L},$$

where y is the current density, and L and M are constants. Goldmann** had previously suggested that the current during illumination, *i.e.*, during the growth, is given by the equation,

$$i = A_1 + B_1 (1 - e^{-m_1 t}),$$

and after the illuminating source had been removed, the decay of the current is represented by the equation,

$$i = A_2 + B_2 e^{-m_2 t},$$

where i represents the instantaneous value of the current at a time t , $m = \frac{1}{cR}$, c being the electrolytic capacity of the cell, R ,

* *Ann. d. Phys.*, 16, 417 (1905).

† *Zeits. phys. Chem.*, 59, 553, 703 (1907).

§ *Jour. Phys. Chem.*, 29, 1406 (1925).

¶ *Phys. Rev.*, 17, 626 (1921).

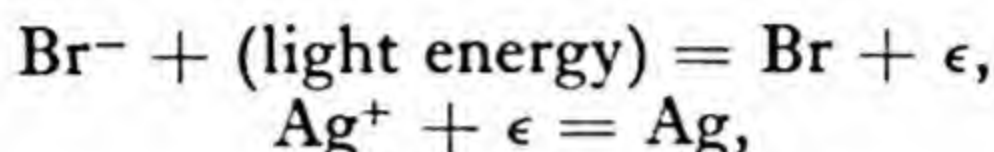
† *Ibid.*, 27, 449 (1908).

|| *Ibid.*, 31, 1357 (1927).

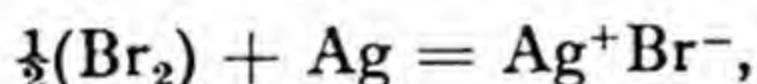
** *Loc. cit.*

the external resistance, and A and B , empirical constants. The values of m_1 and m_2 are not equal, but differ by 40 per cent.

It has been proposed by Sheppard and Trivelli,* and independently by Fajans,† that the photo-chemical effect of light upon silver halide is to discharge an electron from the halogen ion which is then accepted by a silver ion, forming silver atoms and, in the case of bromides, bromine atoms. The former are aggregated to metallic silver and the latter to bromine molecules. This process may be represented thus,



ϵ representing the electron. Supposing this primary action of the light upon the bromine ion to occur in the silver bromide of the photo-voltaic cell, then, at first, both electrons and bromine (as atoms or molecules) may be supposed to move in the direction of the light rays towards the silver electrode. The electrons penetrating into the silver electrode increase the electron pressure and thereby produce the initial surge of negative electricity. Meanwhile, the more slowly moving bromine, on reaching the electrode, attacks it according to the equation,



giving a positive potential.

Vanselow and Sheppard ‡ used two silver-silver bromide electrodes immersed in potassium bromide solutions, the latter saturated with silver bromide. As the concentration of bromine, added to the solution, was increased, the electromotive force of the cell also increased, thus,

Concentration of							
Br (per cent.)	1.0	0.5	0.1	0.05	0.01	0.005	0.001
Steady E.M.F.							
(volt)	0.74	0.66	0.58	0.433	0.285	0.253	0.153

Much work remains to be done in connection with these photo-voltaic cells.

107. Individual ionic heat contents.—Since the electromotive force of a cell is related to temperature according to the equation,

$$E = -\frac{H_v}{\nu F} + T \frac{\partial E}{\partial T},$$

* *Phot. Jour.*, 61, 403 (1921).

† *Zeits. Elektrochem.*, 28, 499 (1922).

‡ *Jour. Phys. Chem.*, 33, 331 (1929).

if values of \mathbf{E} , determined at different temperatures, are plotted against these temperatures, the slope of the resulting curve, at any point, gives $\frac{\partial \mathbf{E}}{\partial T}$ at the corresponding temperature, and we may at once calculate the heat of the cell reaction. This method permits a far more accurate determination of H_v than can be obtained by ordinary calorimetry. Lewis and Randall,* using the cell, $\text{H}_2 | \text{HCl} (0.1\text{M}) | \text{Hg}_2\text{Cl}_2 | \text{Hg}$, obtained a value $-8,291$ calories, per equivalent, for $T \frac{\partial \mathbf{E}}{\partial T}$ at 25°C . Ostwald † assumed that the above equation could be applied to the separate electrode reactions, *i.e.*,

$$\pi = -\frac{H_v}{\nu F} + T \frac{\partial \pi}{\partial T}$$

where H_v is now the heat of ionisation at the single electrode; hence the sum of these heat reactions, *viz.*, those taking place at the electrodes $\text{Pt}, \text{H}_2 | \text{H}^+$ and $\text{Cl}^-, \text{Hg}_2\text{Cl}_2 | \text{Hg}$ is $-8,291$ calories at 25°C . Now $T \frac{\partial \pi}{\partial T}$ is not known for these separate electrode reactions, but if we assume, as we have done, that the value of π for the electrode $\text{Pt}, \text{H}_2 | \text{H}^+$ is zero at all temperatures, then for the electrode reaction, $\text{Cl}^-, \text{Hg}_2\text{Cl}_2 | \text{Hg}$, we have $T \frac{\partial \pi}{\partial T}$ equal to $-8,291$ calories per equivalent. Knowing the value of the electrode potential, π , and that of $\frac{\partial \pi}{\partial T}$, we can then calculate H_v , the heat of ionisation, or the heat evolved when one gram ion is formed at the electrode, by means of the equation,

$$H_v = -\left(\pi - T \frac{\partial \pi}{\partial T}\right) \nu F.$$

It is evident that if the value of $\frac{\partial \pi}{\partial T}$ for the electrode $\text{Cl}^-, \text{Hg}_2\text{Cl}_2 | \text{Hg}$ is known, that for any other electrode may be determined by combining this electrode with the other to form a cell, measuring the value of $\frac{\partial \mathbf{E}}{\partial T}$ for the cell, and taking the value, thus obtained, as being the algebraic sum of the values of $\frac{\partial \pi}{\partial T}$ at the two electrodes.

* *Jour. Amer. Chem. Soc.*, **36**, 1969 (1914).

† See Ostwald, *Lehrbuch der allgemeinen Chemie*, II, 1, 1893.

As a rule, the heat of ionisation is *negative*, or heat is *evolved* when ions are *formed*, and since the heat changes, which occur when one metal displaces another from solutions of its salts, are known from calorimetry experiments, the heat of ionisation, per equivalent, for one metal may be calculated, if that of the other is known.

BIBLIOGRAPHY.

- Auerbach, Zeits. Elektroc., **18**, 13 (1912).
Bauer, Zeits. phys. Chem., **103**, 39 (1922).
Beans and Hammett, Jour. Amer. Chem. Soc., **47**, 1215 (1925).
Blake and Whitney, *ibid.*, **26**, 1339 (1904).
Bodlander and Eberlein, Ber., **36**, 3945 (1903).
Born, Zeits. f. Phys., **1**, 44 (1920).
Bouchet, Comptes Rendus, **188**, 1237 (1929).
Brodsky, Zeits. phys. Chem., **121**, 26 (1926).
Buhl, Phys. Zeits., **28**, 767 (1927).
Cady, Jour. Phys. Chem., **9**, 476 (1905).
Carrara and D'Agostini, Atti. R. Inst. Ven., **62**, 793 (1902).
Carter and Robinson, Jour. Chem. Soc., 267 (1927).
Carveth, Jour. Phys. Chem., **2**, 289 (1898).
Cavanagh, Jour. Chem. Soc., 2207 (1927).
Chow, Jour. Amer. Chem. Soc., **42**, 497 (1920).
Danner, *ibid.*, **44**, 2832 (1922); **46**, 2385 (1924).
Donnan and Allmand, Jour. Chem. Soc., **99**, 845 (1911).
Drossbach, Zeits. Elektroc., **34**, 205 (1928).
Ellis, Jour. Amer. Chem. Soc., **38**, 737 (1916).
Fajans, Ber. phys. Gess., **21**, 249, 709 (1919).
Ferguson and France, Jour. Amer. Chem. Soc., **43**, 2150 (1921).
Féry and Chéneveau, Comptes Rendus, **181**, 606 (1925).
Fosbinder, Jour. Amer. Chem. Soc., **51**, 1345 (1929).
French and Kahlenberg, Trans. Amer. Electroc. Soc., **54**, 163 (1928).
Garrison, Jour. Amer. Chem. Soc., **45**, 37 (1923).
Gerke, *ibid.*, **44**, 1648 (1922).
Getman, *ibid.*, **38**, 792 (1916).
Hainsworth and MacInnes, *ibid.*, **44**, 1021 (1922).
Haring and Bosch, Jour. Phys. Chem., **33**, 161 (1929).
Harned, *ibid.*, **47**, 676 (1925).
Heyrovský, Proc. Roy. Soc., A, **102**, 628 (1923).
Hughes, Jour. Chem. Soc., 491 (1928).
Jones and Dole, Jour. Amer. Chem. Soc., **51**, 1073 (1929).
Kameyama, Phil. Mag., **3**, 235 (1927).
Karpen, Comptes Rendus, **185**, 766, 942 (1927); **186**, 230 (1928).
Kjellin, Zeits. phys. Chem., **77**, 210 (1911).
Knobel, Jour. Amer. Chem. Soc., **45**, 70 (1923).
Koch, Jour. Chem. Soc., 269 (1928).
Krouchkoll, Ann. de Chim. et de Phys., **17**, 129 (1889).
MacInnes and Yeh, Jour. Amer. Chem. Soc., **43**, 2563 (1921).
MacInnes, Adler and Joubert, Trans. Amer. Electroc. Soc., **37**, 383 (1920).
McHenry, Phil. Mag., **3**, 857 (1927).
Meyer, Wied. Ann., **53**, 845 (1894); **56**, 680 (1895).
Mortimer and Pearce, Jour. Phys. Chem., **21**, 275 (1917).
Müller, Zeits. phys. Chem., **65**, 226 (1909).
Neuhausen, Jour. Amer. Chem. Soc., **44**, 1411 (1922).
Neustadt and Abegg, Zeits. phys. Chem., **69**, 486 (1909).
Newbery, Jour. Amer. Chem. Soc., **51**, 1315 (1929).
Niederhauser and Hulett, *ibid.*, **51**, 2327 (1929).

- Noyes and Steinour, Jour. Amer. Chem. Soc., **51**, 1409 (1929).
Pearce and Eversole, Jour. Phys. Chem., **32**, 209 (1928).
Pearce and Farr, *ibid.*, **18**, 729 (1914).
Popoff, Kunz and Snow, *ibid.*, **32**, 1056 (1928).
Prideaux, Trans. Farad. Soc., **25**, 20 (1929).
Richards and Dunham, Jour. Amer. Chem. Soc., **44**, 678 (1922).
Roshdestwensky and McLewis, Jour. Chem. Soc., **101**, 2094 (1912).
Rothmund, Zeits. phys. Chem., **15**, 1 (1894).
Sauer, *ibid.*, **47**, 146 (1904).
Schneider and Braley, Jour. Amer. Chem. Soc., **45**, 1121 (1923).
Schreber, Zeits. Elektroc., **32**, 143 (1926).
Smoluckowski, Handbuch der Elektrizität.
Spooner, Trans. Amer. Electroc. Soc., **38**, 97 (1920).
Svedberg, Colloid Chemistry, 1924.
Taylor, Jour. Phys. Chem., **31**, 1478 (1927).
Veibel, Jour. Chem. Soc., **123**, 2203 (1923).
Vosburgh, Jour. Amer. Chem. Soc., **49**, 2222 (1927).
Vosburgh and Craig, *ibid.*, **51**, 2009 (1929).
Winther, Zeits. phys. Chem., **131**, 205 (1927).
Wosnessensky and Astachow, *ibid.*, **128**, 362 (1927).

CHAPTER VII.

ELECTRO-CAPILLARITY.

108. Electro-capillary effects.—It was shown in the previous chapter that, in general, a potential difference exists at a mercury-electrolyte interface. We may regard the electrical charges as forming a condenser-like *double layer*; the electrical charge, usually positive, spreads over the mercury surface, the electrical forces striving, as it were, to extend the surface area. On the other hand, surface tension effects tend to decrease the surface area, so that if we have an electrical double layer at the surface of contact between mercury and an electrolyte, the net surface tension effect is determined by the natural surface tension of the metal-liquid interface, diminished by the force with which the electrical charge tends to increase the surface area. As this potential difference existing across the interface is decreased, by applying to the interface an opposing potential difference, it is evident that the net surface tension increases and reaches a maximum as the applied potential difference is increased. Finally, it decreases again after the applied potential difference exceeds that of the electrical double layer. We might assume that when this surface tension is a maximum, the measured applied potential difference is equal and opposite to that of the double layer at the interface. This condition of maximum surface tension may be ascertained, experimentally, by means of a *capillary electrometer* of which there are many forms, two being shown in Figs. 36 and 37. Consider the working of the type illustrated in Fig. 36. A mercury reservoir, A, has attached to its lower end a fine capillary jet, B, which dips into a glass vessel, E, at the bottom of which is a mercury electrode, external contact being made with the latter by means of the wire, D. As the bore of B is very small, and the surface tension of mercury high, a long column of mercury can be supported by the surface tension effect. If the double-layer potential at the jet surface is decreased, the interfacial tension increases, and a longer column of mercury can be supported. Since the bore of the capillary jet tapers, as a rule, towards the lower end, the meniscus will move up the tube A until

the upward force due to the surface tension is equal to the downward force of gravity, acting on the column of mercury in A. The meniscus can be brought back to its original position by raising the bulb H. Fine adjustments of H are effected by the rack and pinion, G, the meniscus being watched through the microscope, M.

The solution in E must be saturated with an appropriate mercury salt; for example, if the solution is a chloride, mercurous

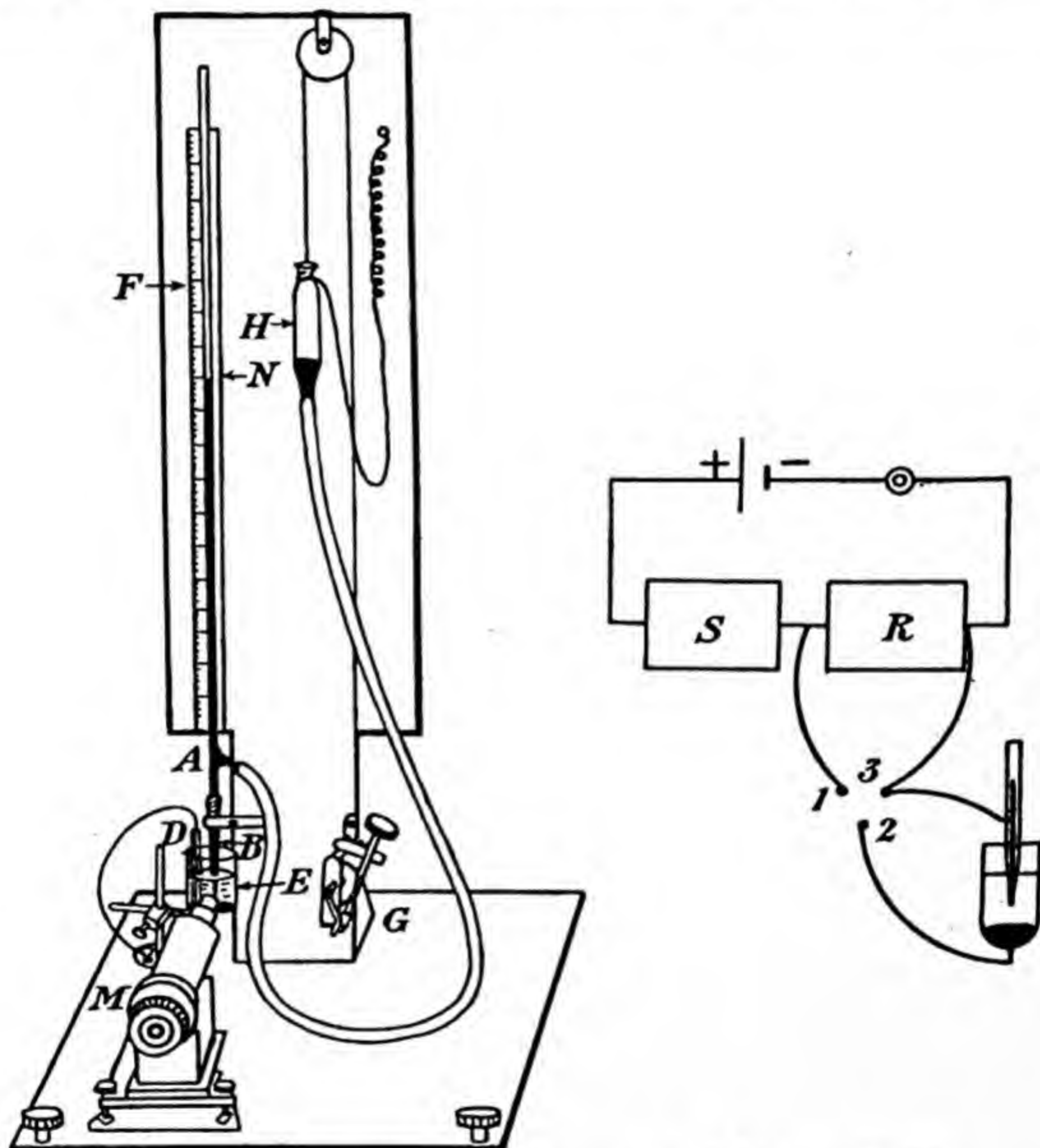


FIG. 36.—A capillary electrometer and connections.

chloride must be used, if a sulphate, mercurous sulphate, *etc.* Mercury ions will then be deposited upon the surface of the jet in B, and thus the mercury in A becomes positively charged. If we wish to neutralise the double layer at this jet surface, the external potential difference must be applied in such a direction that it opposes the double layer potential; *i.e.*, A is connected to the negative terminal of the battery circuit.

In an experiment, the terminals 2 and 3 are joined, so that the mercury electrode in E and the mercury in A are at the same

potential. The position of the meniscus in B is observed. The terminals 2 and 3 are then disconnected, and those of 1 and 2 joined. The total resistance, $R + S$, being maintained constant at, say, 10,000 ohms, R is increased step by step, the position of the upper meniscus, N, being read against the scale, S , for each applied potential difference. The scale readings are then plotted against the applied potential difference, the resulting curve being known as the *electro-capillary curve*. It will possess a maximum, corresponding to maximum surface tension, when the potential of the double layer has been eliminated. Thus, at this point, it is assumed that the applied potential difference is equal, and opposite, to the potential difference, existing under normal conditions, at the mercury-liquid interface. This assumption is not justified, as there are other factors, to be considered later, which influence the surface tension of the mercury-solution interface.

The behaviour of the meniscus in the capillary electrometer is, in general, very different in the ascending portion of the curve from what it is in the descending portion. In the former the mercury is often sluggish, and the surface tension becomes difficult to measure. Further, the surface tension

may take up a certain value immediately after a given potential difference is established between the terminals of the electrometer, and then fall gradually as the time of contact continues. The surface tension corresponding to the descending portion is widely different for solutions with chemically different anions, and even noticeably different for unequally concentrated solutions of the same salt. The *form* of the descending portion for a considerable part of its course is the same (within the limits of experimental error) for equally concentrated solutions of quite different salts, and only varies very slightly for unequally concentrated solutions of a given salt.

Smith * made an exhaustive study of electro-capillary phenomena. In one particular experiment he obtained the electro-

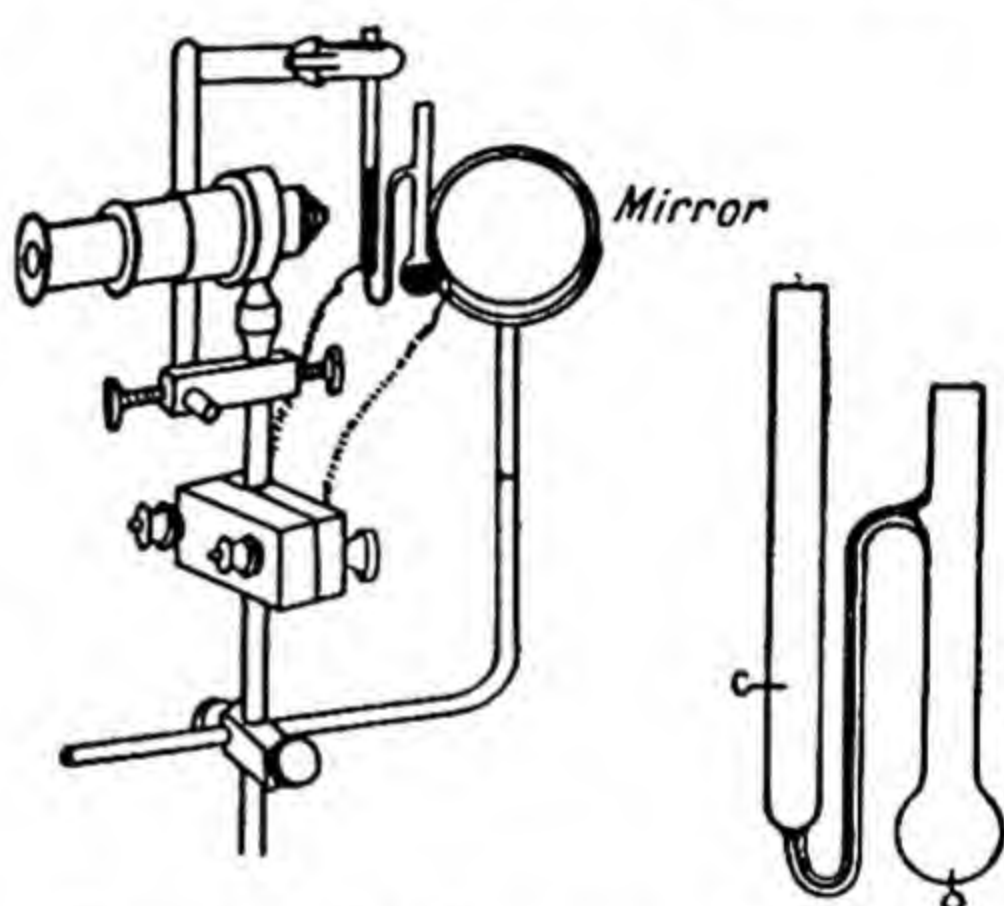
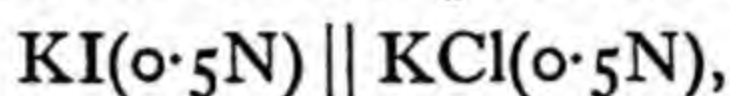


FIG. 37.—Another type of capillary electrometer.

* *Phil. Trans.*, A, 193, 47 (1900).

capillary curve for a 0.5 normal solution of potassium iodide. He then superposed upon this solution a 0.5 normal solution of potassium chloride, and placing the small mercury electrode in this latter solution, determined the electro-capillary curve for this arrangement. When the applied electromotive force exceeded a value of about 0.8 volt the two curves were identical. Since the potential difference at the large electrode was not altered between the two sets of experiments, the potential difference at the small electrode, and therefore the interfacial tension, for an applied electromotive force, greater than 0.8 volt, is the same for both curves. If we assume that the potential of the liquid junction,



can be neglected, and that there are no appreciable potential differences due to concentration changes in the liquid, Smith's results show that below 0.8 volt the surface tension does not depend merely upon the potential difference at the small electrode, but also upon the chemical nature of the solution. Now these solutions are the same in every respect, except that the anion in one is iodide, and in the other, chloride. Until the potential difference, reckoned from the solution to the electrode, reaches a certain value, the effect of the anion upon the surface tension is appreciable, but gradually diminishes, and finally disappears. The applied potential differences at the maximum surface tension in the two cases differ by about 0.2 volt, so that as the liquid junction $\text{KI}(0.5\text{N}) \parallel \text{KCl}(0.5\text{N})$ has a potential difference nothing like as great as 0.2 volt, we see that the highest point of the capillary curve does not necessarily correspond to zero potential difference between the solution and the small mercury electrode.

For a given applied potential difference, the interfacial tension increases as the concentration of the solutions (KCl, KCN) diminishes, and moderately concentrated solutions of KCN give capillary curves of which the maxima lie to the left of the origin, while the weaker solutions give curves in which the maxima are to the right of this point (Fig. 38). If a solution could be found for which the maximum lay at the origin, this would be a null-solution and would exhibit no potential difference with respect to the mercury. Every solution for which the maximum of the electro-capillary curve is at the origin is a null-solution, but the potential differences between mercury and different so-called null-solutions will be different if the maxima for these solutions do not coincide.

The maxima of the curves for KCN solutions are lower than those for the KCl solutions of corresponding strength, and the

horizontal distance between the curves, after they become parallel, is, approximately, 0.125 volt greater than the distance between the maxima. Consequently the solution at the maximum surface tension in KCN is 0.125 volt more positive to the mercury than it is at the maximum in KCl.*

Palmaer,† using the mercury dropping electrode described in section (84), found that by adding certain substances to a 0.1N KCl solution, he could not only reduce the observed potential difference between the still and dropping mercury until it became very small, but could cause it, passing through the value zero, to change in sign. In this way he found two different null-solutions, viz., KCN, KOH and $\text{Hg}(\text{CN})_2$, and H_2S plus a small quantity of

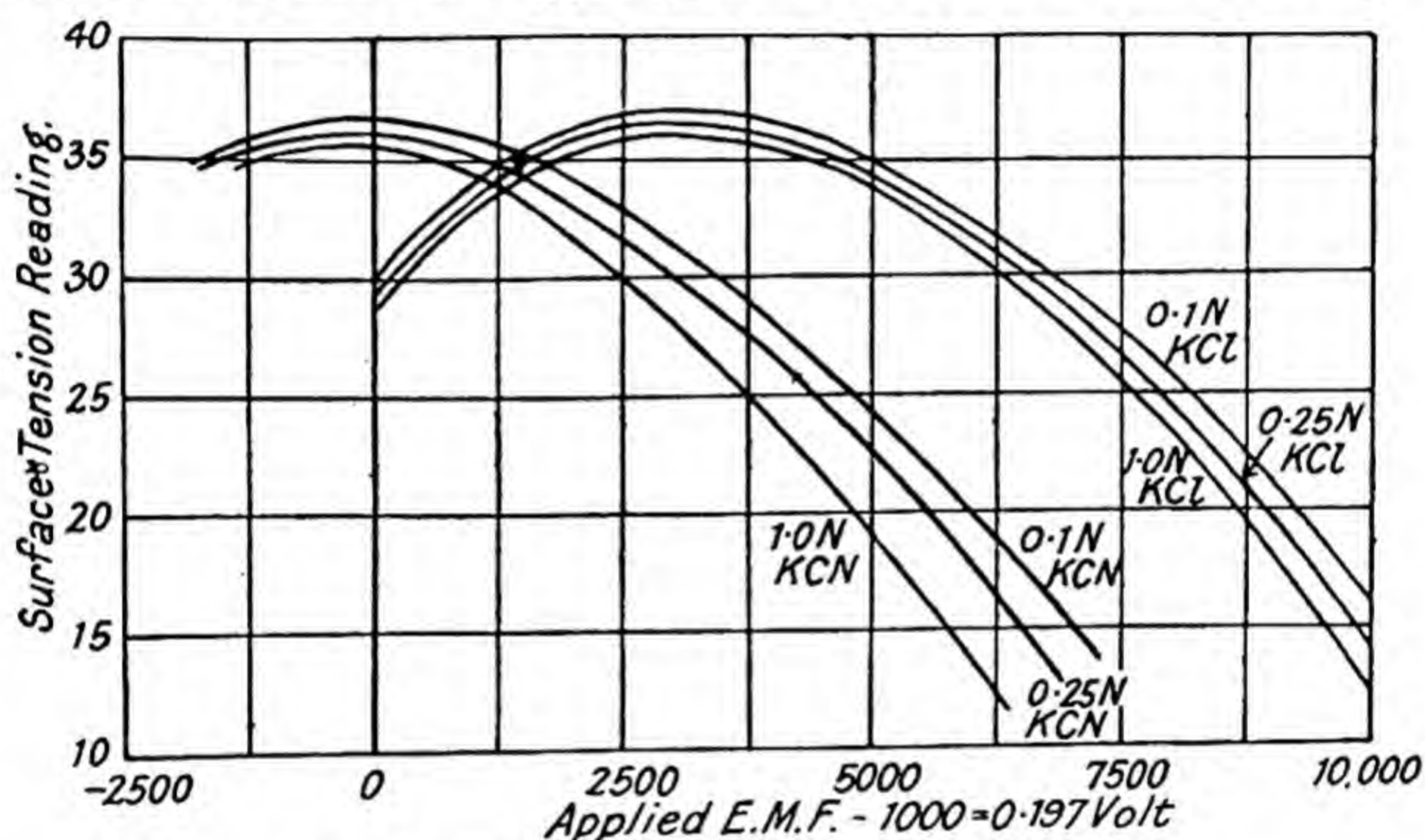


FIG. 38.—Electro-capillary curves. (Smith.)

acetic acid, for which the potential difference between the still and dropping electrodes was zero. Smith and Moss ‡ found several other null-solutions, and showed that the potential difference between mercury and a null-solution is not always the same, and hence is never necessarily zero, as Palmaer assumed.

Smith and Moss compared the results obtained from capillary electrometer and dropping electrode experiments, observing the following quantities :—

- The electro-capillary curve for various potassium cyanide solutions of different strengths.
- The electro-capillary curve for a solution of potassium chloride of equal strength.

* See Smith, *loc. cit.*

‡ *Phil. Mag.*, 15, 478 (1908).

† *Zeits. phys. Chem.*, 59, 129 (1907).

- (c) The horizontal distance between descending branches of two curves.
- (d) The E.M.F. of the cell $\text{Hg} \mid \text{KCN} \parallel \text{KCl} \mid \text{Hg}$.
- (e) The E.M.F. of the dropping electrode circuit $\text{Hg} \downarrow \text{KCN} \mid \text{Hg}$, the measurements being taken when the end of the continuous part of the jet was in the surface of the solution.
- (f) The E.M.F. of the dropping electrode circuit,
 $\text{Hg} \downarrow \text{KCN} \parallel \text{KCl} \mid \text{Hg}$.

Their results are given in Table LIX.

TABLE LIX.
ELECTRO-CAPILLARY MEASUREMENTS.

Strength of Solution.	Maximum Surface Tension. $\text{Hg} - \text{KCN}$. Scale Reading.	Maximum Surface Tension. $\text{Hg} - \text{KCl}$. Scale Reading.	Applied P.D. Corresponding to Maximum Surface Tension. $\text{Hg} - \text{KCN}$.	Horizontal distance between curves (1) and (2). (in volts).	P.D. of $\text{KCN} \parallel \text{KCl} \mid \text{Hg}$ (volts).	P.D. of $\text{Hg} \downarrow \text{KCN} \parallel \text{Hg}$ (volts).	P.D. of $\text{Hg} \downarrow \text{KCN} \parallel \text{KCl} \mid \text{Hg}$ (volts).
0.1N	36.65	36.75	0.039	0.645	0.642	0.043	0.679
0.2N	36.30	36.70	0.020	0.667	0.671	0.018	0.694
0.24N	36.10	36.53	0.010	0.687	0.687	0.012	0.698
0.25N	36.08	36.35	0	0.691	0.690	0.003	0.699
0.26N	36.04	36.30	0	0.696	0.693	— 0.001	0.697
0.27N	36.00	36.27	— 0.005	0.697	0.696	— 0.005	0.693
0.50N	35.81	36.17	— 0.020	0.716	0.715	— 0.016	0.703
1.0N	35.70	36.10	— 0.059	0.748	0.745	— 0.046	0.705

Solutions of potassium cyanide and potassium chloride of equal strengths being, approximately, of the same electrical conductivity and degree of ionisation, the contact potential difference between them will be very small. This is confirmed by the agreement between the numbers in columns (4) and (5). Each number in column (7) should equal the sum of the corresponding ones in columns (5) and (6). Also, by comparing the numbers in columns (3) and (6), it is seen that Paschen's* relation holds, namely, that the potential difference required to produce the maximum surface tension between mercury and an electrolyte is equal, in many cases, to the electromotive force of the corresponding dropping-electrode circuit. The relation fails immediately when the chemical action at the dropping electrode, due to atmospheric oxygen, becomes appreciable. The "Paschen" electro-

* *Wied. Ann.*, 41, 42 (1890).

motive force between mercury and a solution of potassium chloride remains unchanged on the addition to the solution of small quantities of sodium sulphide, although the natural potential difference between mercury and the solution is thereby altered by more than half a volt.

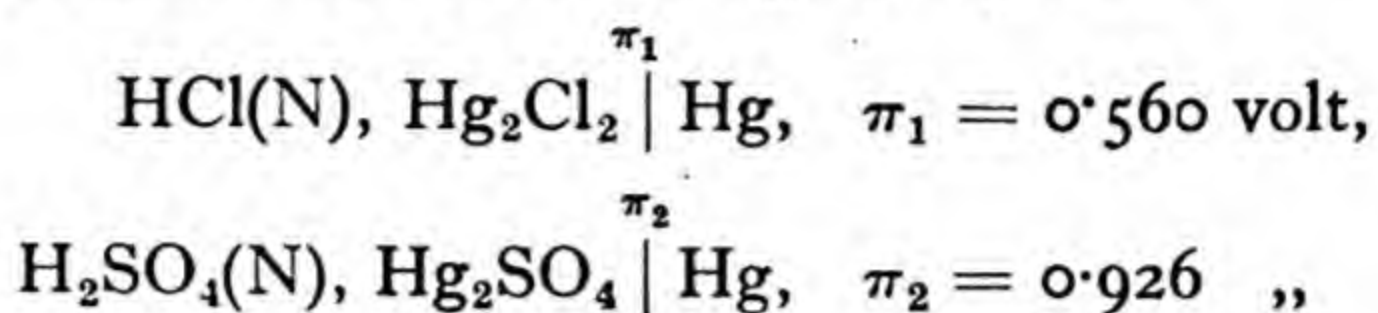
109. Theoretical considerations.—It has been shown in **section (16)** that the surface tension of an interface depends upon the concentration and nature of the solute in the solvent. Substances which *raise* the surface tension are known as *capillary inactive*, and those which *depress* it are termed *capillary active*. Now the capillary-active substance not only lowers the maximum surface tension, and therefore the maximum point of the electro-capillary curve, but also displaces the curve to the right or left, the direction of displacement depending upon which of the ions, anions or kations, are active. The actual direction may be predicted in the following manner. If the anions alone are active, that surface of the electrical double-layer which falls in the solution will be decidedly richer in anions than it would be if they were inactive. Hence the interfacial tension, and therefore the rising branch of the curve, is strongly depressed, as is also the region of the maximum.*

Corresponding to the falling branch of the curve the inactive kations predominate in the solution surface-layer, so that the depression produced by the anions disappears, and the curve then coincides with that found for capillary-inactive electrolytes. But at the maximum point of the curve no change in the surface tension, and therefore no change in the concentration of the solution, can occur upon a change in the potential difference, and so the mercury surface must carry a negative charge at the maximum point in order to balance the tendency of the anions to adsorption which, if it occurred, would change the concentration of the solution. The case of capillary-active kations is exactly the converse, both the falling branch of the curve and its maximum are strongly depressed, and the mercury must have a positive charge at the maximum point. Thus it follows that the applied potential difference, required to produce the maximum surface tension, is equal to the absolute potential of the mercury only when capillary inactive solutions are used. In such cases there is zero potential difference between the small mercury

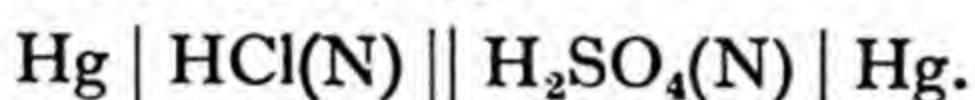
* Throughout the rising portion of the curve the mercury in the jet is positive to the solution, and therefore the mercury surface is relatively rich in positive ions, while the other surface of the double layer must be negatively charged, *i.e.*, it contains an excess number of anions.

electrode and the solution, at the point corresponding to maximum surface tension.

If we consider a cell containing capillary inactive solutions, its electromotive force is equal to the difference of the electrode potentials (neglecting any liquid-liquid junction potentials), and this sum is given by the horizontal distance between the maxima of the electro-capillary curves for the two solutions. This conclusion is confirmed in the following example :—

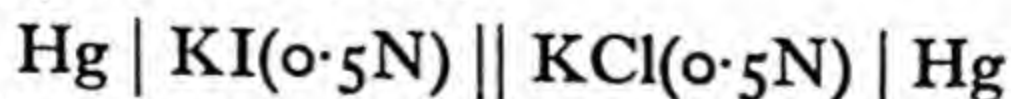


where π_1 and π_2 are the potentials corresponding to the maximum surface tension. The horizontal distance between the maxima of the curves corresponds, therefore, to 0.366 volt, and this should be the value of the E.M.F. of the cell



Actually the E.M.F., as measured by potentiometer methods, is 0.3669 volt.

This reasoning cannot be applied to capillary active solutions, but, as mentioned above, an active ion exerts its disturbing influence only on one part of the electro-capillary curve. An active anion does not affect the descending part of the curve, so that if we consider the curves for two solutions containing different active anions, the descending parts of the curves correspond with those which would be obtained if these solutions were capillary inactive. Thus, the horizontal distance between the descending branches of the two curves is determined entirely by the different mercurous ion concentration, and is equal to that which would be obtained over the whole course of the curves if the solutions were inactive. It should, therefore, be equal to the E.M.F. of a cell, consisting of mercury electrodes in contact with these two solutions. For example, in the cell



the horizontal distance between the descending branches of the curves for the two solutions corresponds to 0.399 volt, whereas the measured E.M.F. of the cell is 0.394 volt.

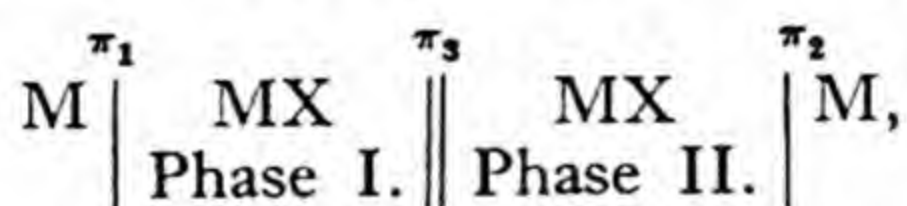
110. Electro-capillary phenomena at other interfaces.—Various investigators * have measured the electro-capillary curves

* See Rothmund, *Zeits. phys. Chem.*, 15, 1 (1894); Meyer, *Wied. Ann.*, 53, 845 (1894); 56, 680 (1895).

for amalgams. Now amalgams of metals less noble than mercury behave, as regards their interfacial potential difference, like pure metals when their metal content exceeds a certain amount. As long as the metal does not react with the solution, the applied potential difference, necessary to produce the maximum surface tension, should be equal to the potential difference between the metal and the solution in question. Amalgams actually give, in electrolytic solutions, electro-capillary curves similar to those of mercury, and the expected relation is fulfilled to a considerable degree for metals such as lead, bismuth and copper.

If one phase dealt with at a liquid-liquid boundary is a metal, matters are comparatively simple. Theoretically, because only one kind of ion, the kation for preference, *i.e.*, the kation of the metal in question, passes from one phase into the other. At the boundary of two other liquids, say an aqueous solution and an organic liquid, one must, on the other hand, take into account the transference and distribution of all the various ions present.

Few experiments have been made in this direction. Krouchkoll* and Kandidow† set up a capillary electrometer, using ethyl ether saturated with uranyl nitrate as one phase, and an aqueous solution, also saturated with the same substance, as the other phase. They found an electro-capillary curve with a maximum when the positive electrode dipped into the aqueous solution, and the negative into the ethereal solution. Wild‡ determined the electro-capillary curves for various electrolytic solutions in different non-aqueous solvents. The electrode potentials, π_1 , π_2 , of the chain



formed by shaking an aqueous solution of MX with a second non-aqueous solvent until distribution was attained, have been deduced from the electro-capillary curves. The results show that in all cases $\pi_1 = \pi_2$. Since the phase potential, π_3 , equals $\pi_1 + \pi_2$, it follows that π_3 is either zero or exceedingly small, less than 5-10 millivolts. While this conclusion holds for all solvents, it is by no means certain that it is true for all ions.

111. Theories of electro-capillarity.—Two theories have been put forward to account for the changes in the surface tension of mercury, produced by the application of a potential difference across the interface. According to Lippmann the effect is to be

* *Ann. de Chim. et de phys.*, 17, 129 (1889).

† *Zeits. phys. Chem.*, 83, 587 (1913).

‡ *Ibid.*, 103, 1 (1922).

regarded as a purely electrostatic one, due to the tendency of the electrical charge at the surface to expand so as to reduce the surface tension. On the other hand, the variation in the surface tension is also attributed to the change in the concentration of the mercury ions near the interface, brought about by the applied potential difference.

Considering Lippmann's theory first, we may imagine that a surface area increase, δA , is accompanied by an increase, δQ , in the charge residing on the mercury surface, so that if the potential of the electrolyte be reckoned as zero, and that of the mercury, π , the change, δE , in the energy of the "double layer condenser," formed by the opposite charges at the interface, is given by

$$\delta E = S\delta A + \pi\delta Q,$$

where S is the interfacial tension. But $Q = cA\pi$, where c is the capacity per unit area. Thus,

$$\delta Q = c\pi\delta A + cA\delta\pi,$$

or

$$\delta E = (S + c\pi^2)\delta A + cA\pi\delta\pi.$$

Since δE is a perfect differential,

$$\frac{\partial}{\partial A}\left(\frac{\partial E}{\partial \pi}\right)_A = \frac{\partial}{\partial \pi}\left(\frac{\partial E}{\partial A}\right)_\pi,$$

or

$$\frac{dS}{d\pi} = -c\pi,$$

the minus sign indicating that S decreases as π increases. Integrating, we have

$$S = S_0 - \frac{1}{2}c\pi^2, \quad . \quad . \quad . \quad (139)$$

where S_0 is the surface tension arising from the non-electrical distribution of energy. Equation (139) gives the relation between the observable surface tension and the potential difference at the mercury surface. If the only effect of the potential difference is to produce an electrostatic surface energy, represented by $\frac{1}{2}c\pi^2$ per unit surface area, then the observed surface tension should have a maximum at $\pi = 0$, even though c may be variable. It must be remembered, however, that the observed variation in the surface tension need not be due solely to a variation in $\frac{1}{2}c\pi^2$. The non-electrical surface energy, represented by S_0 , may vary with the potential difference. A variation in the potential difference at the interface may be accompanied, not only by a variation in the electrostatic surface energy, but also by a variation in the

distribution of the matter in the neighbourhood of the surface, and it seems that we cannot consider the phenomena as if they were due to a certain non-electrical distribution, upon which is superposed an electrostatic double layer, the latter producing no other effect than that represented by its electrical energy. Hence the maximum surface tension may not correspond to zero potential difference, since the maximum surface tension may arise from the fact that non-electrical effects, accompanying the change in the potential difference, and tending to reduce the surface tension, pass through a minimum value as the potential difference changes. This minimum value need not necessarily correspond to zero potential differences.

Equation (139), which is of parabolic form, is the equation of the electro-capillary curve. From the approximate parabolic nature of some of the curves (Fig. 38), through a considerable portion of their course, the Lippmann theory leads, not only to the view that throughout a considerable range the capacity per unit area is constant, but also makes it possible for the value of this capacity to be calculated. Assuming the specific inductive capacity of the dielectric of the double layer to be unity, theory allows, further, an estimate to be formed of the distance between the parallel charges forming the double layer. Also, since $Q = cA\pi$, equation (139) may be written thus,

$$\frac{\partial S}{\partial \pi} = - \frac{Q}{A} = Q_0 \times 10^7,$$

where Q_0 is the charge, measured in coulombs, on the double layer, per square centimetre, and π is expressed in volts.

According to Gibbs,* the interfacial potential difference brings about a change in the concentration of the mercury ions about the electrode, and we may therefore use the principles of **section (16)** to investigate electro-capillary phenomena.

Consider a closed surface, drawn about the portion of the mercury solution interface at which the conditions are to be investigated, containing parts of the two homogeneous phases, *i.e.*, metal and solution, and cutting the non-homogeneous parts, where the phases merge into each other, normally to the interface. The volume within this surface can be divided into two parts by a dividing surface, drawn parallel to, and sensibly coincident with, the actual surface. According to Gibbs, any constituent of a system, in equilibrium, must have the same thermodynamic potential in all phases of which it is a component. Hence, when

* *Scientific Papers*, Vol. II.

equilibrium has been established across the interface separating a metal and an electrolyte containing its ions, the thermodynamic potential, \mathbf{F}^+ , of the metallic ions must be the same in both phases, *i.e.*, on either side of the dividing surface. If, at the instant when the metal comes into contact with the electrolyte, it is not at the electrical potential necessary for equilibrium, the thermodynamic potential of the metal ions in the two phases will differ, and consequently some of them will pass from the phase in which their potential is higher to that in which it is lower. In order to preserve equilibrium, when the electrical potential of the mercury is changed by $\delta\pi$, the thermodynamic potential of the mercury ions in the solution must change by $\delta\mathbf{F}_{\text{Hg}^+}$, where

$$\delta\mathbf{F}_{\text{Hg}^+} = q_{\text{Hg}^+}\delta\pi, \quad . \quad . \quad . \quad (140)$$

q_{Hg^+} being the charge in coulombs on the gram ion. An increase in the concentration of the mercury ions will be accompanied, in general, by an adjustment in the concentration of the electrons in order to preserve electrical neutrality, and so, for the electrons,

$$\delta\mathbf{F}_e = q_e\delta\pi. \quad . \quad . \quad . \quad (141)$$

Hence, from equation (37),

$$\delta S = - C_{\text{Hg}^+}\delta\mathbf{F}_{\text{Hg}^+} - C_e\delta\mathbf{F}_e, \quad . \quad . \quad (142)$$

where C_{Hg^+} and C_e represents the concentrations, in gram-equivalents per square centimetre, of the mercury ions and electrons, respectively, and S is the surface tension when the superficial concentrations remain constant. Thus, from equations (140), (141) and (142),

$$\frac{\partial S}{\partial \pi} = - C_{\text{Hg}^+}q_{\text{Hg}^+} - C_eq_e. \quad . \quad . \quad (143)$$

The values of C_{Hg^+} and C_e depend upon the position of the dividing surface. Consider it to be placed so that the excess of the mercury ions on the mercury side of the interface is zero, *i.e.*, the electrical charge upon the mercury is equal to the superficial excess, or deficiency, of electrons upon it. Other ions, represented by x , y , *etc.*, present in the solution, may be adsorbed at the mercury surface, but since, on the whole, the separating surface is electrically neutral,

$$C_{\text{Hg}^+}q_{\text{Hg}^+} + C_eq_e + C_xq_x + C_yq_y = 0.$$

If no mercury ions are specifically adsorbed, the charge of the excess electrons on the mercury side of the interface is equal, and opposite, to the charge of the excess mercury ions in the solution.

Schofield * placed the dividing surface where the concentration of the mercury ions is zero, so that, from equation (143),

$$\frac{\partial S}{\partial \pi} = -C_e q_e,$$

from which we obtain an expression, similar to that deduced from Lippmann's theory, namely,

$$\frac{\partial S}{\partial \pi} = Q_0 \times 10^7.$$

Butler,† however, has pointed out that a choice of position of the dividing surface, which makes C_{Hg+} , or C_e , zero, tends to an illusory result, for under these conditions $C_{Hg+}q_{Hg+}$, or $C_e q_e$, cannot be identified with Q_0 , the charge on the double layer.

When mercury ions are adsorbed at the surface, $C_{Hg+}q_{Hg+} + C_e q_e$ is not necessarily zero, since we now have an additional surface density of mercury ions at the surface above that corresponding to the electron charge, $C_e q_e$, this additional amount consisting of

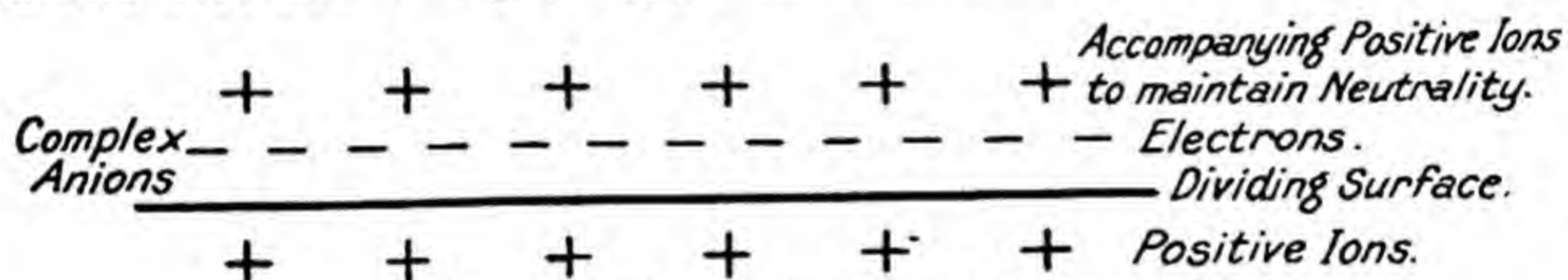


FIG. 39.—Electro-capillary adsorption.

complex anions coming from the solution. The electrical double layer now assumes a complex nature because, in order to preserve electrical neutrality in the interface as a whole, the excess number of complex anions must be accompanied by an equivalent amount of positive ions. The double layer will thus be of the form shown in Fig. 39, and the electrical work, done during the adsorption of the anions, may be much less than that corresponding to the total potential difference across the interface.

Gouy,‡ and Frumkin,§ have developed theories which are combinations of Lippmann's theory and Gibbs's relation for the lowering of the surface tension by adsorbed substances. Frumkin's equation is

$$\delta S = -C_{Hg+}q_{Hg+}\delta\pi - \sum C_i \delta F_i,$$

in which the first term represents the normal effect, and the second the effect of the adsorption of capillary active ions, F_i

* *Phil. Mag.*, 1, 641 (1926).

† *Proc. Roy. Soc., A*, 113, 594 (1927).

‡ *Ann. d. Phys.*, 7, 129 (1917).

§ *Zeits. phys. Chem.*, 103, 55 (1923); *Zeits. f. Phys.*, 35, 792 (1926).

being the thermodynamic potential, in the superficial layer, of ions of the i th kind. A similar expression has also been developed by Rice.* Since C_i is, in general, a function of π , the equation is only a partial expression for the change of surface tension with potential difference, and its integration demands a knowledge of the relation between C_i and π .

Butler † shows that Gibbs's equation, by itself, is inadequate to account for the electro-capillary curve anomalies, and holds that an electrostatic effect should also be included. From his theory he deduces the relation,

$$\frac{dS}{d\pi} = -2Q_0 - C_{\text{Hg}}q_{\text{Hg}} - \sum \frac{d}{d\pi} \int C_i dF_i,$$

in which the first term represents this electrostatic effect, while the second and third terms represent the effects of the adsorbed mercury ions, and of other adsorbed ions or molecules, respectively. C_i itself varies with π , and can be calculated only by kinetic methods. The equation accounts quantitatively for the electro-capillary curves in iodide solutions, and qualitatively for all types of curves exhibited by salt solutions.

Krüger ‡ also explains the anomalies of the electro-capillary curves on the adsorption theory, and shows that the anomaly increases with increasing stability of the corresponding complex salts. This relationship, however, does not hold generally, since the stability of complex salts increases in the following order, nitrates, sulphates, iodides and cyanides, whereas the maximum surface tensions of mercury in normal solutions of the nitrate, sulphate, iodide and cyanide of potassium are 98.95, 100.17, 94.0 and 96.6 C.G.S. units, respectively.

In the absence of active ions, we should expect surface tension measurements to yield the same potential differences at the junctions Hg | KI, Hg | KCl, provided that the solutions are of the same ionic concentration. Since the potentials are not equal, it is assumed that complex anions are adsorbed at the Hg | KI junction, but not at the other, the difference in the maxima of the electro-capillary curves being attributed solely to this adsorption effect.

Similarly, although a mercury dropping electrode is at the same potential as the surrounding liquid, if the latter contains no active ions, it will certainly have a potential, different from that of the liquid, if active ions are present, the actual electrical charge upon unit area of the mercury surface in this case being the same

* *Jour. Phys. Chem.*, 30, 1501 (1926).

† *Zeits. Elektrochem.*, 19, 681 (1913).

‡ *Loc. cit.*

as that which the mercury surface possesses in the maximum surface tension state. In the dropping-electrode experiment the fresh mercury surface not only takes up, or gives off, mercurous ions, but also adsorbs capillary active ions, if present, both anions and kations. At the point of entry of the jet there is a tendency towards a state in which the charge on the mercury balances the adsorption of similarly charged active ions.

Summarising, we may say that in capillary inactive solutions true single potential differences may be determined, both from the electro-capillary curve and by means of the dropping electrode. This is not the case if the solution contains any capillary active substance, both methods yielding the same deviation.

Liebreich * found that with several electrolytes the maxima of the capillary curves correspond with the formation of hydroxides at the mercury surface. Further, immediately after the maximum is passed, hydrogen gas is generated which frees the surface from the hydroxides. Hence the negative branch of the curve corresponds with a bright metallic mercury surface, and the positive branch, and the maximum, with a surface coated with hydroxides or basic salts. The cleansing of the surface begins at the maximum. He assumes that the anomalies of the curves are related to this phenomenon. Such a connection may possibly lie in a diminution of the surface tension by partial solution of the hydroxides, or basic salts, in the mercury, or, more probably, in adsorption of the anions in question.

Schofield † has measured the amount of mercurous sulphate adsorbed at a mercury surface in contact with an electrolyte containing this salt, and found that it corresponds with that calculated, from surface tension measurements, by means of Gibbs's adsorption equation. He identified the number of mercurous ions, adsorbed at a freshly expanded interface, with the number of ions which, on the Nernst theory of electrode potential, are deposited on the mercury interface, and impart to it their charge. He suggests that the surface charge may be set up by a retreat of electrons from the surface, *i.e.*, by a flux of electricity across the interface. The flux may in turn be regarded as producing at the surface, in accordance with Faraday's law, the same quantity of mercurous sulphate as would be adsorbed from solution if no electrical flux had taken place.

112. The absolute zero of potential.—As we have seen, the Lippmann-Helmholtz theory of electro-capillarity postulates

* *Zeits. Elektroc.*, 32, 162 (1926).

† *Loc. cit.*

that, at the maximum interfacial tension, the electrical double-layer vanishes. However, modern ideas of molecular orientation at liquid-liquid boundaries, due to molecular dipoles, necessarily lead to the view that, at the surface of uncharged mercury, a new double layer, due to the adhesive layer of solvent, or ions, must arise. We can thus never eliminate the electrically charged layers, and the idea of an absolute zero of potential becomes meaningless.

From capillary electrometer and dropping-electrode experiments the absolute potential of the normal calomel electrode is taken to be about 0.56 volt, with the mercury positively charged. On the other hand, Billitzer* tried to obtain the absolute zero by an entirely different method. Metals are ordinarily charged negatively when suspended in water. By adding substances to the water, Billitzer caused the metal to become positively charged, and took the condition, when the metal had no charge, as indicating zero potential difference between the metal and the solution. According to these results, the potential difference of the normal calomel electrode would be about 0.18 volt, with the mercury negatively charged. In other words, the point of zero potential is displaced about 0.74 volt towards the oxygen end of the scale of absolute potential.

Billitzer's results have been criticised by Blake,† and by Goodwin and Sosman,‡ but work by Garrison§ has confirmed Billitzer absolutely, as far as measurements are concerned. Heyrovský|| also believes that the absolute zero of potential is, approximately, 0.8 volt in error. Bodforss¶ found a value 0.4 volt for the normal calomel electrode, with the mercury positively charged.

With a discrepancy of from 0.7 to 0.8 volt for the absolute potential zero, between two methods, for which the experimental error does not exceed a few hundredths of a volt, the only possible explanation is that two different quantities are being measured. This is the solution proposed by Smoluckowski,** and accepted both by Freundlich†† and Svedberg.‡‡ Thus, although electrocapillary phenomena suggest that the absolute zero potential occurs at, approximately, — 0.28 volt, *i.e.*, 0.28 volt below the

* *Zeits. Elektroc.*, 8, 638 (1902); *Ann. d. Phys.*, 11, 902 (1903); *Zeits. phys. Chem.*, 45, 327 (1903); 48, 513, 542 (1904).

† *Jour. Amer. Chem. Soc.*, 26, 1378 (1904).

‡ *Phys. Rev.*, 21, 129 (1905).

§ *Jour. Amer. Chem. Soc.*, 45, 37 (1923).

|| *Proc. Roy. Soc., A*, 102, 628 (1923).

¶ *Zeits. Elektroc.*, 29, 121 (1923).

** Graetz, *Handbuch der Elektrizität* (1914).

†† *Kapillar-Chemie* (1923).

‡‡ *Colloid Chemistry* (1924).

potential of the normal hydrogen electrode, the absolute zero potential cannot be definitely fixed.

113. Electro-kinetic phenomena.—An externally applied electromotive force may produce a displacement of a liquid along a boundary surface ; for example, across a diaphragm, or along a capillary tube. This effect is known as *electro-endosmosis*. Perrin * suggested that the inner wall of such a capillary tube became coated, as it were, with an electrical double layer, one charge being on the liquid in immediate contact with the glass, and the other on the glass, so that an external potential difference, applied between the ends of the tube, causes the movable inner layer to be displaced relatively to that upon the walls, its direction of motion depending upon the sign of the electrical charge. We may regard this double layer as a condenser charged to a certain potential difference. In pure water the wall, for the great majority of solids, is charged negatively with respect to the movable water, and therefore the latter moves towards the negative pole in capillaries of glass, quartz, and shellac, and through diaphragms of clay, carborundum, asbestos, *etc.* Among the many factors which influence electro-endosmosis may be mentioned the applied electromotive force, the kind and arrangement of the diaphragm, the kind and concentration of the electrolytes present, and the temperature.

Perrin found that the negatively charged diaphragms became more negative when an alkali was added, and less negative with the addition of an acid, or salt. With increasing acid concentration they became neutral and, finally, positive in sign. He also found that, in general, the greater the valence of the kation of an added salt, the greater was the decrease in the potential difference between this type of diaphragm and the solution ; and the greater the valence of the anion of an added salt, the greater was the decrease in the potential difference between the diaphragm and the solution.

The rate of electro-endosmosis flow through a capillary tube is given by the equation,

$$v = \frac{i\pi D}{4\pi\eta\sigma},$$

where v is the volume of liquid which passes a cross-section of the tube in unit time, π , the potential difference of the double layer, D the dielectric constant of the medium within this layer, η the coefficient of viscosity of the liquid, i , the electric current and σ the specific conductance.

If electro-endosmosis takes place in such a way that a difference

* *Jour. Chim. Phys.*, 2, 601 (1904) ; 3, 50 (1905).

of level results, the hydrostatic pressure, p , which will be established, is given by the equation,

$$p = \frac{2\pi DE}{A},$$

E being the applied electromotive force, and A the cross-section of the tube.

The phenomenon of *cataphoresis*, the reverse of electro-endosmosis, is the movement of solid particles against a liquid; *i.e.*, solid particles, suspended in a liquid, will migrate, under the influence of an applied electromotive force, to one, or other, of the electrodes, according as they are positively or negatively charged. When small quantities of some electrolytes are added to suspensions cataphoresis ceases, the colloidal particles in suspension coagulate, and are precipitated. The ions which are most effective in causing precipitation are those having an electrical charge opposite in sign to that carried by the suspended particle, and the precipitating action is greater the higher the valence of the ions.

The velocity, u , with which a suspended particle moves through a liquid towards an electrode is given by the equation,

$$u = \frac{\pi DE}{4\pi\eta l},$$

where l is the distance between the electrodes.

Electro-kinetic phenomena are widely utilised in various commercial processes.

BIBLIOGRAPHY.

- Bennewitz and Delyannis, *Zeits. phys. Chem.*, **30**, 1306 (1926).
 Billitzer, *Zeits. Elektroc.*, **8**, 638 (1902); *Ann. d. Phys.*, **11**, 902 (1903); *Zeits. phys. Chem.*, **45**, 327 (1903); **48**, 513, 542 (1904).
 Bodforss, *Zeits. Elektroc.*, **29**, 121 (1923).
 Butler, *Proc. Roy. Soc. A*, **122**, 399 (1929).
 Chapman, *Phil. Mag.*, **25**, 475 (1913).
 Colange, *Comptes Rendus*, **186**, 74 (1928).
 Dubrisay, *ibid.*, **181**, 1142 (1925).
 Freundlich, *Kapillar-chemie* (1923).
 Freundlich and Rona, *Sitz. Preuss. Akad.*, 397 (1920).
 Freundlich and Wreschner, *Koll. Zeits.*, **28**, 250 (1921).
 Frumkin and Gorodetzka, *Zeits. phys. Chem.*, **136**, 215 (1928); 451 (1928).
 Ghosh, Chaudhuri and Sen, *Jour. Ind. Chem. Soc.*, **1**, 189 (1924).
 Goodwin and Sosman, *Trans. Amer. Electroc. Soc.*, **7**, 83 (1905); *Phys. Rev.*, **21**, 129 (1905).
 Gouy, *Ann. d. Phys.*, **7**, 129 (1917).
 Herzfeld, *Phys. Zeits.*, **21**, 28 (1920).
 Kandidow, *Zeits. phys. Chem.*, **83**, 587 (1913).
 Kleeman and Simonds, *Phys. Rev.*, **21**, 38 (1923).

- Krüger, Zeits. Elektroc., 17, 465 (1911) ; 19, 681 (1913).
Krüger and Krimreich, *ibid.*, 19, 617 (1913).
Rosenberg and Stegeman, Jour. Phys. Chem., 30, 1306 (1926).
Sand, Trans. Farad. Soc., 5, 159 (1909).
Seith, Zeits. phys. Chem., 117, 257 (1925).
Smith, Phil. Mag., 5, 398 (1903).
Stern, Zeits. Elektroc., 30, 508 (1924).
Takeuchi and Akashi, Phys. Math. Soc. Japan Proc., 8, 192 (1926).
Talmund, Kolloid Zeits., 48, 164 (1929).
Wild, Zeits. phys. Chem., 103, 1 (1922).

CHAPTER VIII.

POLARISATION.

114. Polarisation.—Theoretically, every cell reaction is reversible with infinitely small currents, but, in practice, there are very few examples in which an experimentally determined electromotive force is equal to the reversible electromotive force, for measurable currents. To pass a finite current through a cell, the applied electromotive force must be greater than the reversible value, even after due allowance is made for the potential difference required to overcome the electrical resistance. This difference, produced by electrolysis, is known as *polarisation*.

In some cases the cause of polarisation is evident. Thus, when an electric current is passed between copper electrodes, immersed in copper sulphate solution, copper goes into solution at the anode, and is deposited from the solution at the cathode. Accordingly, there are concentration changes in the immediate vicinity of the electrodes, these changes giving rise to an electromotive force which is opposed to that applied. To pass an electric current through the cell, work equivalent to that required to produce these concentration changes must be performed. The cell now yields an opposing electromotive force termed *concentration polarisation*. The concentration changes may occur, not only in the layer of electrolyte in contact with the electrode, but also in the surface layers of the electrode adjacent to the electrolyte. Reactions such as this, in which the small changes that occur may be attributed to concentration changes in the electrolytic boundary layer, are reversible, as, for example, the discharge of hydrogen ions at platinised platinum, giving rise to hydrogen gas, the electro-deposition of metals from their simple salts, oxidation and reduction processes, $\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++}$, and the anodic solution of many metals in different electrolytes.

The reversibility of any electrode is limited, in practice, by the concentration polarisation that occurs when any appreciable quantity of electricity is passed across the metal-liquid interface. There are cases, however, where the observed polarisation is too great to be explained solely on the basis of concentration changes.

Thus, when electricity is passed between platinum electrodes, immersed in dilute sulphuric acid, oxygen gas is produced at the anode and hydrogen at the kathode. Even before any visible gas bubbles have formed, very small amounts of these gases are liberated and adhere to the platinum, either in the form of a condensed layer on the surface, or, actually in solution in the metal. The platinum plates, neutral to begin with, are thus transformed into oxygen and hydrogen electrodes, and are said to be polarised. If, now, the decomposing current is stopped, and the two electrodes joined by a wire, the arrangement yields an electric current, which passes in the opposite direction to the original, or charging, current. It originates from the polarisation effects, the gases which cling to, or have penetrated into, the plates, giving rise to the current. As soon as the gases disappear, it ceases.

115. Back electromotive force.—Polarisation may be studied by using a gas cell of the type shown in Fig. 40, applying

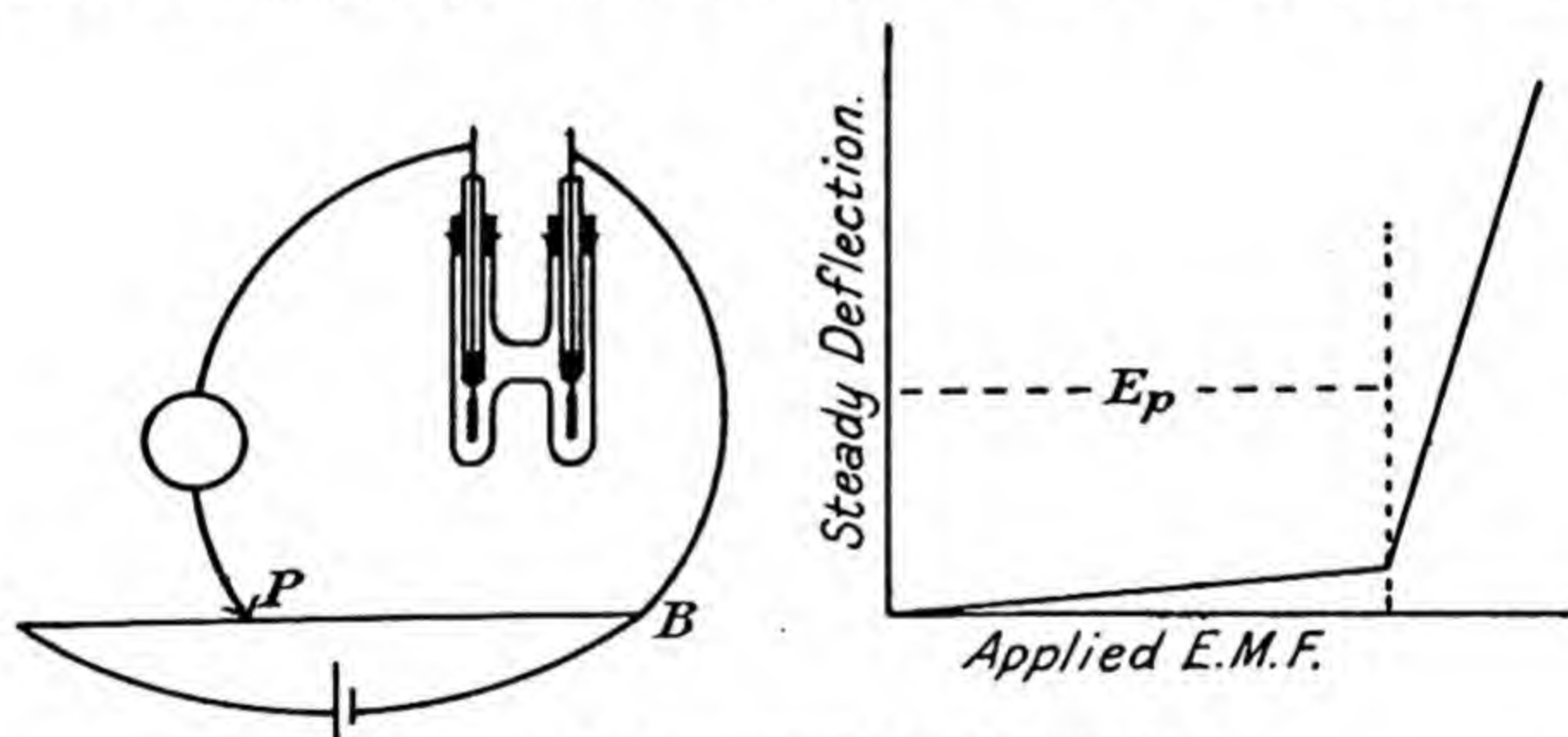


FIG. 40.—Measurement of polarisation.

a gradually increasing potential difference to the cell from the potentiometer, and noting the relation between the current flowing and the applied potential difference. Thus, if the contact, *P*, is near *B*, so that a small potential difference is imposed on the cell, the galvanometer shows an initial deflection which rapidly decreases practically to zero. The current does not cease altogether. Oxygen and hydrogen both being soluble in water, pass slowly off from the electrodes into the electrolyte. There they may either escape into the atmosphere, or recombine. The polarisation of the plates therefore slowly disappears of its own accord, or would do so, but for the fact that it is maintained by the renewed action of the applied electromotive force. The small steady current, indicated by the galvanometer, is the value required to maintain

the polarisation that is being dissipated, and is usually called the residual current.

The galvanometer deflection increases slowly with the imposed electromotive force, until the latter reaches a certain critical value, E_d . When once this critical value is passed, the current rises rapidly with any further increase in the applied electromotive force. E_d is equal to the opposing electromotive force plus the product of the electrolytic resistance and the residual current. As the latter is extremely small, we may take E_d to be approximately equal to this opposing, or *back electromotive force*, E_p . The latter may be determined, experimentally, by allowing the current from the battery to flow for a few minutes, and noting the value of the potential difference across the electrodes of the gas cell, immediately the primary current is shut off.

If the gas cell contains platinum electrodes immersed in dilute sulphuric acid, and the imposed electromotive force is raised to about 1.11 volt, the platinum electrodes become saturated with oxygen and hydrogen, respectively, and any further electrolysis will be without effect in this direction. In effect, oxygen and hydrogen electrodes have been formed with definite potentials and, accordingly, the back electromotive force has reached a stationary value. The latter corresponds to the energy change in the reaction, $H^+ + OH^- \rightarrow H_2O$, and may be described as the theoretical, or reversible, electromotive force of the cell. It is independent of the addition of acids and alkalis to the water. Thus, according to the mass action law,

$$[H^+][OH^-] = K[H_2O],$$

where $[H^+]$, $[OH^-]$ and $[H_2O]$ represent the concentration of the hydrogen ions, hydroxyl ions and water, respectively. Since the concentration of the water remains practically constant, we have

$$[H^+][OH^-] = \text{constant},$$

so that if the value of $\log [H^+]$ is increased, by adding acid, that of $\log [OH^-]$ must be decreased by an equal amount. But the electromotive force of the hydrogen-oxygen cell is proportional to $\log [H^+]$ plus $\log [OH^-]$, and, therefore, the electromotive force between the two electrodes is independent of the values of $[OH^-]$ and $[H^+]$.

Kohlrausch * showed that the difference of potential, E , between the electrodes of an electrolytic cell through which a current, i , is passing, is given by the equation,

$$E = Ri + P \int i dt,$$

* See Kohlrausch and Holborn, "Leitvermögen der Elektrolyte."

where R is the ohmic resistance of the electrolyte, and P is a function which depends both upon the nature and the size of the electrodes, and the nature of the electrolyte, but is independent of E . This relationship is similar to that which would be expected



FIG. 41.—Polarisation effects.

if we had a circuit of two condensers of capacity c_1 and c_2 , respectively, placed in series with a resistance R , as shown in Fig. 41. In this arrangement, if E , E_1 , E_2 , O represent the potentials of the various condenser plates, then,

$$E - E_1 = \frac{1}{c_1} \int i \, dt,$$

and
$$E_2 = \frac{1}{c_2} \int i \, dt.$$

Since
$$E_1 - E_2 = Ri,$$

we have
$$E = Ri + \left(\frac{1}{c_1} + \frac{1}{c_2} \right) \int i \, dt,$$

which is identical in form with Kohlrausch's equation, if P is equal to $\frac{1}{c_1} + \frac{1}{c_2}$.

We may suppose that when an electric current passes through the electrolyte, gas is adsorbed at the surface of the metal electrodes, this adsorbed gas layer acting as the dielectric of a condenser. If the electromotive force applied to the cell is small, electric charges exist on the opposite faces of these condenser-like layers, although, since the condensers are probably very "leaky," there will be a "leakage current" through them, and so through the electrolyte. As the electromotive force is increased, the potential gradient across the adsorbed gas film becomes too great for the charges to remain as they were, and the anions and the cations are actually deposited upon the electrodes. This deposition point corresponds to the sudden change in the galvanometer deflection as the electromotive force is increased.

116. Decomposition voltage.—The value of the applied potential difference at which the current suddenly increases, and

continues to rise proportionately to the potential difference, is known as the *decomposition voltage*. At this stage deposition of the anions and the cations, *i.e.*, separation of the ions, occurs, and since this decomposition voltage is approximately equal to the back electromotive force, which, in turn, is equal to the algebraic sum of the potential difference at the electrode-liquid interfaces, it follows that the decomposition voltage must exceed the sum of the electrode potentials.

The value of a decomposition voltage may be determined experimentally in two ways. If the potential difference applied to a solution is greater than the opposing electromotive force, the circuit may be broken, the opposing electromotive force measured by means of a voltmeter, and the result is the required decomposition voltage. An alternative method is to gradually increase the current through the solution and plot corresponding values of the current and applied potential difference. That value of the latter at which a sudden increase in the current occurs is the decomposition voltage.

Le Blanc,* using platinum electrodes in normal solutions of salts from which the metal was deposited, obtained the results given in Table LX. It will be observed that, whereas the values

TABLE LX.
DECOMPOSITION VOLTAGES.

Electrolyte.	Decomposition Voltage. (Volts.)	Electrolyte.	Decomposition Voltage. (Volts.)
Zinc sulphate .	2.35	Perchloric acid .	1.65
Zinc bromide .	1.80	Pyrotartaric acid .	1.57
Cadmium chloride	1.88	Trichloroacetic acid	1.51
Cadmium sulphate	2.03	Hydrochloric acid	1.31
Cadmium nitrate	1.98	Hydrazoic acid .	1.29
Nickel chloride .	1.85	Oxalic acid .	0.95
Nickel sulphate .	2.09	Hydrobromic acid	0.94
Silver nitrate .	0.70	Hydriodic acid .	0.52
Lead nitrate .	1.52	Ammonium	
Cobalt chloride .	1.78	hydrate .	1.74
Cobalt sulphate .	1.92	Methylamine $\left(\frac{N}{4}\right)$	1.75
Sodium hydroxide	1.69	Diethylamine $\left(\frac{N}{2}\right)$	1.68
Potassium hydroxide .	1.67	Tetramethyl	
Sulphuric acid .	1.67	ammonium	
Nitric acid .	1.69	hydrate $\left(\frac{N}{8}\right)$.	1.74
Phosphoric acid .	1.70		
Monochloroacetic acid .	1.72		

* *Zeits. phys. Chem.*, 8, 299 (1891) ; 12, 333 (1893).

for metallic salts vary from metal to metal, those for acids and alkalis are never above 1.67 volts, corresponding with the separation of hydrogen and oxygen at the platinum electrodes. Acids and alkalis, which evolve hydrogen and oxygen on electrolysis, have this maximum decomposition potential, nearly independently of the solution concentration. For acids which are more easily decomposed, the numbers increase on dilution, and there is a simultaneous change in the nature of the products.

117. Overvoltage.—If an electric current is passed for about half an hour between platinum electrodes, immersed in dilute sulphuric acid, and the circuit is then broken, it is found that a potential difference of about 1.1 volts exists between the electrodes. The latter have become saturated with hydrogen and oxygen gas, respectively, and the potential difference represents the theoretical, or reversible, electromotive force of the gas cell. On the other hand, if acidulated water is electrolysed, the potential difference that must be applied before visible gas evolution, in the form of bubbles, commences, is always greater than this value, and varies with the nature of the electrodes between which the solution is electrolysed. A definite excess voltage over the thermodynamically reversible value is required, and this excess is known as the *overvoltage*, or *overpotential*.

Unfortunately, a confused nomenclature is used in connection with this phenomenon. When a current traverses an electrolytic cell, the total potential difference, E , between its terminals may be subdivided into several components. There is first the potential drop, iR , due to the resistance of the liquid, and secondly, a voltage, E_0 , corresponding to the chemical reaction accompanying the current. This voltage, E_0 , can be calculated from Helmholtz's equation (107). If the current is stopped, and the electrodes connected to an electrostatic voltmeter, yet another voltage, E_p , is observed. Some authors have used the term overvoltage to indicate $E - iR - E_0$, others prefer to regard $E_p - E_0$ as the overvoltage. As a rule, it is usual to take as the definition of this phenomenon, the potential, in excess of the reversible electrode potential, necessary to discharge the gas at the electrode, both potentials being measured under identical conditions as regards the external pressure, the temperature and the concentration of the solution. The term has been extended to mean the difference in potential between a reversible gas electrode and the test electrode at which the same gas is being liberated in the same electrolyte at some definite current density. Thus, the hydrogen overvoltage on a lead kathode, at a given current density, will

be the potential difference between that lead kathode and the solution, when hydrogen is evolved at the kathode, less the potential difference between a reversible hydrogen electrode (in practice platinised platinum with no current flowing) and the same solution at the same temperature and pressure. For example, one would expect that the evolution of hydrogen gas would begin at the kathode as soon as the potential of the latter is depressed below zero volt; actually it begins at -0.005 volt, if the kathode consists of platinised platinum. With a zinc kathode it does not commence until the kathode potential, relative to the solution in contact with it, is -0.7 volt. This value is the overpotential of hydrogen evolution upon the zinc surface.

Overpotential should be distinguished clearly from polarisation, the gradual change in potential with current density. The ordinary type of polarisation can be made negligibly small if we carry out the electrode reaction slowly, *i.e.*, with a small current density, but overpotential is quite different. It cannot be eliminated by working with small currents. Until the kathode potential of zinc, for instance, is 0.70 volt below the equilibrium potential, hydrogen gas is not produced at all in the form of bubbles. At this point, what we may term a kind of supersaturation of the zinc with hydrogen becomes so great, that the gas is freely evolved.

Caspari * first studied overvoltage quantitatively, and many other investigators have measured it for various electrodes under different physical conditions.

118. Measurement of overvoltage.—Opinion is divided as to the proper method of measuring overvoltage experimentally, especially when high current densities are used. Two distinct methods have been employed, namely, (1) the *direct method*, in which the electrode potential is determined while the current is flowing, and (2) the *commutator method*, where the current is periodically interrupted by means of a rapidly rotating commutator, and the electrode is connected to a potentiometer only during the period of interruption. In either case the measurements are made against a normal hydrogen electrode, or some other type of standard electrode.

Any correct method of measurement must fulfil the first two, and if the current is interrupted, all of the following requirements, namely, (1) neither the size, nor the shape of the containing vessel, nor the distance between the anode and kathode should exert

* *Zeits. phys. Chem.*, 30, 89 (1899).

any influence; (2) by definition, the value found must represent a potential difference and not a resistance; this entails the elimination of appreciable potential drops due to resistance of the electrolyte, or any resistance at the electrode surface; (3) if the measurement is made while the current is interrupted, the back electromotive force must be instantaneously constant, and have the same value as when the exciting current is forming; there should be no potential fall during the interruption period.

To measure the overvoltage at various metals, the anode and the kathode must be separated in such a way that the possibility of contaminating the kathode with anode material, or with electrolyte from the anode compartment, should be reduced to a minimum. One form of apparatus used by Harkins and Adams *

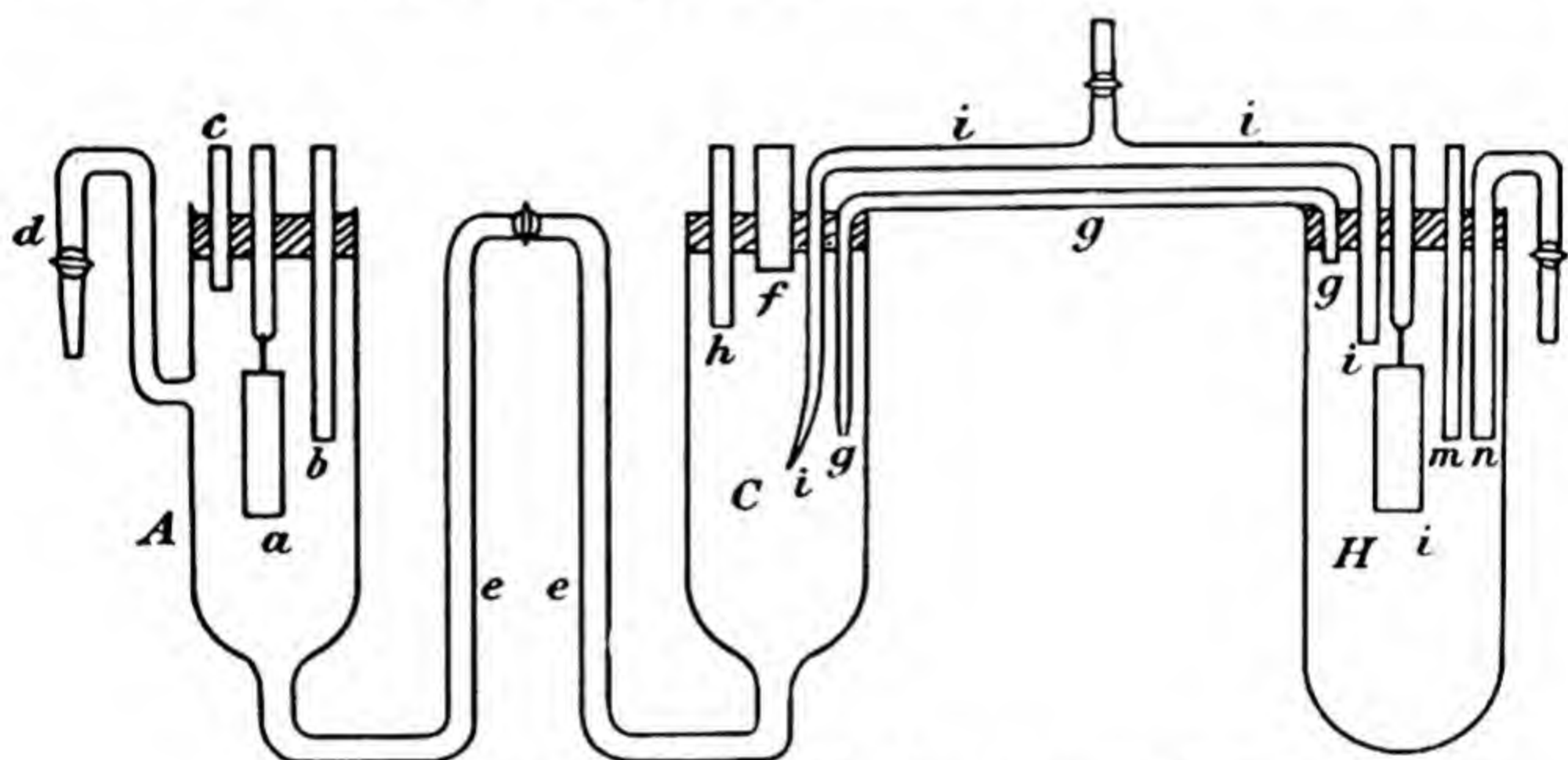


FIG. 42.—Measurement of hydrogen overvoltage.

in the measurement of overvoltage is shown in Fig. 42. The anode compartment, A, contained a hydrogen electrode, *a*, as the anode. Hydrogen gas could enter through the tube *b* and escape by way of the outlet *c*, and the electrolyte could be withdrawn through the side tube *d*. Connection with the kathode compartment, C, was provided by means of the large glass tube *e*, bent in the manner indicated. This kathode compartment contained a glass tube, *f*, through which the various kathodes under observation could be introduced, and removed, without disturbing any part of the apparatus. Hydrogen passed from the hydrogen compartment, H, into the kathode compartment through the tube *g* and escaped by way of the tube *h*. A third tube, *i*, drawn out into a capillary jet, formed one arm of the bridge.

* *Jour. Phys. Chem.*, 29, 205 (1925).

Hydrogen could be passed into the compartment H, through the tube *m*, and out through the tube *g*. The capillary end of *i* was brought into contact with the kathode in C and the fall of potential between the hydrogen electrode H and the kathode, as measured by means of a potentiometer, gave the overvoltage.

In the usual commutator method of measuring overvoltage, one segment of the commutator connects the polarising current for a definite time interval, and after breaking the current, another segment connects the potentiometer for an equal time interval. Unless the overvoltage is constant after disconnecting the electrolysing current, the potentiometer must of necessity measure an average of the potential, and give a value without any meaning. One type of commutator, as used by Knobel,* is shown in Fig. 43. It consisted of a two-piece shaft, the parts being insulated from each other by the hard rubber bearing, C. A wheel, A, controlled

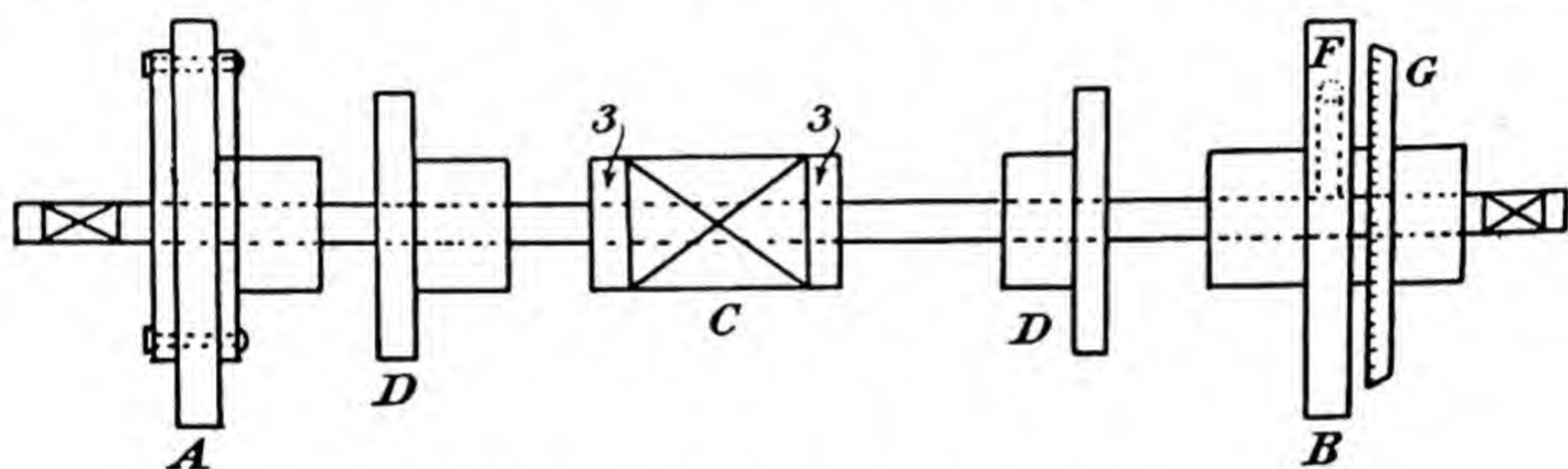


FIG. 43.—Knobel's commutator for overvoltage measurements.

the electrolysing current and a strip of phosphor bronze served as a brush. A slip ring, D, was used as a return connection for the current. Connection was made with the potentiometer circuit by means of a point contact, F, on the hard rubber wheel, B. This wheel could be turned on the shaft so that F might make contact at any desired phase relation with respect to the contact of the current on A. Thus, by successive adjustments of B with respect to A (read on the scale G) the overvoltage at any desired time after the current was made, or broken, could be obtained. In practice, the time taken for the overvoltage to decrease to zero is greater than that which elapses between switching on a current and the overvoltage attaining its maximum value. Accordingly, arrangements must be made so that the current is off for a longer period than that during which it flows. In Knobel's apparatus this was effected by means of a secondary contact device geared to the shaft.

* *Jour. Amer. Chem. Soc.*, 46, 2613 (1924).

119. Comparison of the methods of measuring overvoltage.—It is interesting to compare the values of the overvoltage, as determined by the direct and commutator methods. Tartar and Keyes,* using the apparatus shown in Fig. 44, measured the overvoltage at kathodes of different metals by both methods.

The experimental cell, A, was connected to the cell electrolyte contained in C by means of the capillary connection, B, the saturated potassium chloride solution in D, forming a bridge for the normal calomel electrode, E. The manner in which the commutator, F, connected the polarising current, and then communicated the potential of the kathode in A to the potentiometer, P, is evident from the figure. S was a standard cell, K, a key,

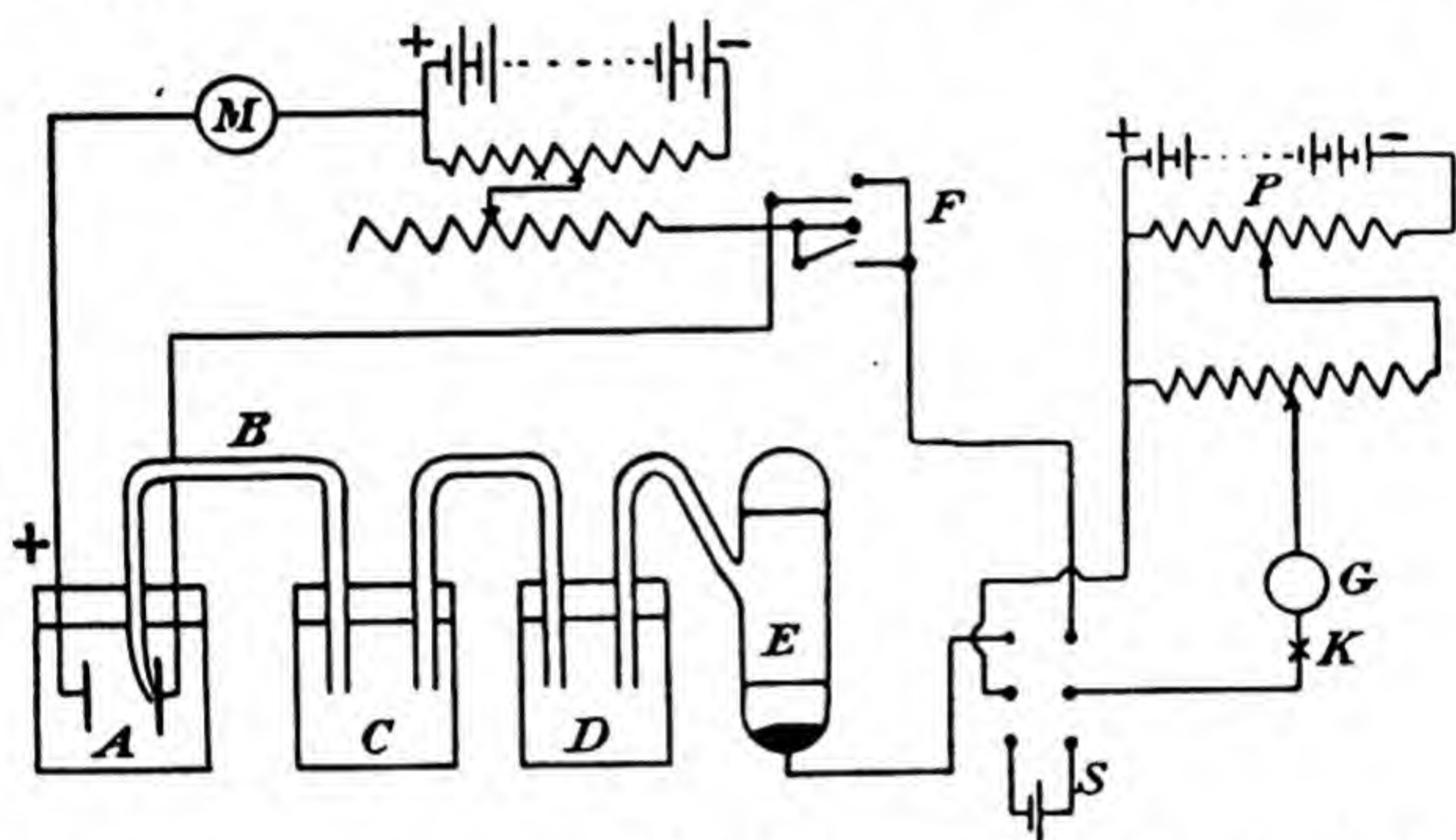


FIG. 44.—The measurement of kathode overvoltage, commutator and direct methods.

and M, a milliammeter by means of which the polarising current was read. The results which these experimenters obtained for various metals, using a lead anode and 0.5 normal sulphuric acid, are given in Table LXI.

Under conditions which afford reproducible values of polarisation, there is a wide divergence between the values given by the direct and commutator methods, and it is fairly obvious that the quantities measured are not the same. The smaller values, given by the commutator method, are considered by Newbery † to be a correct measure of overvoltage, the higher values, obtained by the direct method, being attributed to the existence of an ohmic

* *Jour. Amer. Chem. Soc.*, 44, 557 (1922).

† *Jour. Chem. Soc.*, 125, 511 (1924).

TABLE LXI.

KATHODE OVERVOLTAGES MEASURED BY THE DIRECT AND COMMUTATOR METHODS.

Current Density amps./sq. dcm.	Pt.-Platinum.		Nickel.		Copper.		Iron.	
	Com- mutator (volt).	Direct (volt).	Com- mutator (volt).	Direct (volt).	Com- mutator (volt).	Direct (volt).	Com- mutator (volt).	Direct (volt).
0.26	0.011	0.011	0.238	0.312	0.456	0.563	0.248	0.290
0.39	0.010	0.015	0.235	0.324	0.454	0.619	0.297	0.431
0.64	0.015	0.020	0.240	0.356	0.475	0.690	0.354	0.584
1.27	0.018	0.022	0.275	0.432	0.475	0.832	—	—

resistance (the so-called *transfer resistance*) which is included in the directly measured polarisation. Other workers have ascribed the divergence of the results to errors inherent in the commutator method, contending that it does not measure the overvoltage in the accepted sense of the term. It seems to be established that the difference is due, in part, to the very rapid fall in potential which occurs when the polarising current is interrupted. In the case of hydrogen overvoltage, the maximum concentration of the gas within the surface layer of the electrode will be less when the current is interrupted, than when it is continuous, since, in the former case, greater opportunity is afforded for the removal of the hydrogen by such processes as diffusion and chemical reaction. Newbery found that the directly measured values always increased with the current density, whereas those determined by means of the commutator method actually decreased for certain metals. Another important factor to be considered in the commutator method is that the speed of the commutator decides the period during which the current flows, or is cut off, and the measured value of the overvoltage will vary with this time interval. In addition, the induced electromotive forces, arising from the make and break of the current, will lead to a reduction of the overvoltage.

Glasstone,* working with the commutator method and small time intervals between the make and break of the current, measured the potential of the polarised electrode at 0.002 second, 0.004 second, 0.006 second, and 0.012 second after the current was cut off. He then plotted the potentials, thus obtained, against the time interval, and by extrapolating the curve to zero time, determined the potential of the electrode at the instant when the current was cut off. His results, shown below, prove

* *Jour. Chem. Soc.*, 123, 2926 (1923).

that, even in the first $\frac{1}{500}$ part of a second after the polarising current has been stopped, there is a considerable fall in the potential of the polarised electrode :—

Time after Switching Off Current. (Second.)	Lead Kathode in N Sulphuric Acid. (Volts.)	Copper Kathode in N Sulphuric Acid. (Volt.)
0.002	0.91	0.345
0.004	0.87	0.320
0.006	0.84	0.300
0.012	0.80	0.270
extrapolated	1.02	0.395

He also found that, by applying the extrapolation method to the overvoltage measurements with lead, mercury, copper, iron and nickel electrodes at very small current densities, the extrapolated value was almost identical with that obtained by the direct method. For higher current densities the two values diverged by amounts which increased with the current density, and depended upon the size of the electrode. His results indicate that with low current densities the direct method is the simplest one to use when measuring the true overvoltage, in fact, it is the only one available, whereas at higher current densities the commutator method is more satisfactory.

120. Kathodic overvoltage.—Unfortunately, the same electrode will give different overpotential values at different times, and the discrepancy between the values obtained by different experimenters, who have used different methods of measuring it, is very great. For example, Newbery * found that the overvoltage was erratic, especially in acid electrolytes, rising rapidly at first, and then falling to much lower values after repeated subjection to high current densities. Some of his results, obtained for the cathodic overvoltage on different metals, are as follows :—

Platinum.—The overvoltage in acids is very low and steady, but unless the surface is platinised, the time effect is very great, especially at low current densities. After continued use with high current densities the surface is automatically platinised, and it is then difficult to raise the overvoltage above the low value.

Copper.—The overvoltage is fairly steady and low, but is susceptible to traces of impurity in the electrode, or in the electrolyte, such impurities usually tending to lower the overvoltage. In alkaline electrolytes it is decidedly higher than in acids, and it also tends to increase with time at the higher current densities.

Gold.—In this case the overvoltage is more constant than that on copper. When the electrode is deposited in a spongy

* *Jour. Chem. Soc.*, 109, 1051 (1916).

condition from a solution of the sulphate, the overvoltage is very low.

Lead.—This metal is capable of acquiring a very high overvoltage, but the latter is easily destroyed unless considerable care is exercised. The application of a high current density is sufficient permanently to lower the overvoltage to 0.55 volt in acid electrolytes, but in alkalis the overvoltage is raised by similar treatment.

Zinc.—This metal has an overvoltage as great, or greater than, that on lead, and it has the advantage that the high overvoltage is not destroyed, but rather increased, by subjection to the action of high current density. In many respects it is decidedly preferable to lead as a kathode for powerful reductions.

Nickel.—It is very difficult to lower the overvoltage on this metal. Roughening the surface, or depositing a thin coating of silver on the metal, depresses the overvoltage for a time, and interrupting the current for a few seconds causes a temporary fall in the overvoltage, but it rapidly rises to a still higher value on renewing the current.

Cobalt.—This metal has an overvoltage of the same order as that on nickel in acid electrolytes, but it is much more constant. In alkalis, the overvoltage is, at first, a little higher than that on nickel, and gradually increases with time. At very high current densities sudden rapid rises of overvoltage take place, and these higher values persist at all current densities.

Tin.—The overvoltage is lower than, but similar to, that on lead. It is permanently lowered in acid electrolytes by the action of high current densities.

Aluminium.—When first used it has a fairly high overvoltage in acid electrolytes, but when subjected to a high current density the overvoltage suddenly falls.

Mercury.—This metal has a variable overvoltage. Newbery found that sometimes, after the current had been passing at fairly high density for long periods, the overvoltage would suddenly decrease. Ellingham* suggested that this is due to an alteration in the electrode surface. After using mercury as the kathode for long periods of time, and then breaking the current, bubbles of gas may be observed rising at the metal surface. In alkalis the overvoltage attains very high values for a short time only, but in these cases it is known that an alkali-amalgam is formed.

* See *Trans. Farad. Soc.*, 19, 825 (1924).

Amalgamation raises the overvoltage on all metals, but there is always a slight fall of overvoltage as the mercury sinks into the metal surface.

Bismuth and antimony.—These metals have similar values for the overvoltage. In acid electrolytes the cathodic overvoltage on bismuth is very erratic, but in alkaline electrolytes it is steady.

121. Anodic overvoltage.—Overpotential also occurs at an anode in cases of electrolysis where the evolution of oxygen gas occurs. It is rather difficult to determine, directly, the potential at which oxygen, in the absence of overpotential, ought to be evolved, but it has been shown* that the equilibrium potential of an oxygen electrode in an acid of normal hydrogen ion concentration is $+1.23$ volts. Under ordinary conditions it is necessary to apply a higher potential than this value before oxygen evolution in bubbles occurs. Newbery found the following characteristics for the oxygen overpotential with different metals:—

Gold.—This metal has a high anodic overvoltage which, in acids, is steady and fairly constant. The maximum value is reached at a comparatively low current density. In alkalis the overvoltage is much higher, and the maximum value occurs at a high current density.

Platinum.—In acid electrolytes the overvoltage on platinum after the first few minutes is almost unalterable, either by time, or current density. In alkali electrolytes the overvoltage resembles that on gold in that it rises slowly with time, and it also shows a sudden large increase when the current density is increased.

Copper.—This metal is strongly negative to an oxygen electrode at all current densities.

Silver.—At low current densities Newbery found that a silver electrode dissolved slowly in acid electrolytes, and the potential of the metal remained negative with respect to an oxygen electrode. In alkalis silver is attacked at low current densities, the surface becoming rapidly coated with black oxide, and the electrolyte discoloured. The anodic overvoltage is not high in acids or in alkalis, but a silver anode may be used for oxidations in some cases in the presence of substances which readily reduce silver oxides.

Lead.—Both in acids and in alkalis a lead anode rapidly becomes coated with the dioxide at moderate current densities, but at all current densities the metal shows a strong positive potential to an oxygen electrode after the dioxide coating has formed.

* See Nernst, *Zeits. Elektrochem.*, 11, 835 (1905).

While the coating is forming, the overpotential rises steadily, and finally reaches a very constant and high value after the coating has attained a thickness approaching 0.1 mm.

Nickel.—This metal becomes "passive," *i.e.*, it will not transmit the current, when the current density is equal to, or greater than, 100 milliamperes per square centimetre. In alkalis pure nickel is "passivated" at once, even at the lowest current densities. The anodic overvoltage is low and fairly constant, and it has similar values in acids and in alkalis.

Cobalt, unlike nickel, cannot be passivated in dilute sulphuric acid, although the value of its potential approaches that of an oxygen electrode with very high current densities. In alkalis passivity is produced immediately.

Iron.—In dilute sulphuric acid iron requires a high current density to passivate it. In alkaline solutions passivity is induced in a few seconds, even at the lowest current densities.

Tin.—In acid electrolytes tin shows no sign of passivity, but it readily becomes passive in alkaline solutions. The overvoltage rises to a very high value, but it is very erratic.

Carbon.—The overvoltages on graphite and other carbons are very variable in both acid and alkaline solutions.

122. Experimental results.—Knobel, Caplan and Eiseman* have given a complete set of values for the hydrogen and oxygen

TABLE LXII.

HYDROGEN OVERVOLTAGE AT 25° C.

Current Density. M.A. per Sq. Cm.	Overvoltage (Volts) on													
	Au.	Cd.	Cu.	Platinised Pt.	Smooth Pt.	Al.	Graphite.	Ag.	Sn.	Fe.	Zn.	Bi.	Ni.	Pb.
0.0	—	0.47	—	0.00	—	—	0.00	—	0.24	0.20	—	—	—	—
0.1	0.12	0.65	0.35	0.00	—	0.50	0.32	0.30	0.40	0.22	—	—	—	—
1.0	0.24	0.98	0.48	0.02	0.02	0.57	0.60	0.48	0.86	0.40	0.72	0.78	0.56	0.52
2	—	—	—	0.02	0.03	0.63	0.65	0.58	0.95	0.45	0.73	—	0.63	—
5	0.33	1.09	0.55	0.03	0.05	0.75	0.73	0.69	1.03	0.50	0.73	0.98	0.71	1.06
10	0.39	1.13	0.58	0.03	0.07	0.83	0.78	0.76	1.08	0.56	0.75	1.05	0.75	1.09
50	0.51	1.21	—	0.04	0.19	0.97	0.90	0.83	1.19	0.70	0.93	1.15	0.89	1.17
100	0.59	1.22	0.80	0.04	0.29	1.00	0.98	0.87	1.22	0.82	1.06	1.14	1.05	1.18
200	0.67	1.23	0.99	0.04	0.36	1.18	1.08	0.94	1.23	0.99	1.17	1.20	1.13	1.22
500	0.77	1.25	1.19	0.04	0.57	1.24	1.12	1.03	1.24	1.26	1.20	1.21	1.21	1.24
1000	0.80	1.25	1.25	0.05	0.68	1.29	1.22	1.09	1.23	1.29	1.23	1.23	1.24	1.26
1500	0.81	1.26	1.27	0.05	0.77	1.30	1.22	1.08	1.23	1.29	1.24	1.29	1.25	1.29

* *Trans. Amer. Electroc. Soc.*, 43, 55 (1923).

overvoltages, on different metals, at 25° C. They used the direct method of measurement, and take, as the definition of overvoltage, the potential necessary in excess of the reversible potential to discharge the gas in question. Their results are shown in Tables LXII. and LXIII.

TABLE LXIII.

OXYGEN OVERVOLTAGE AT 25° C.

Current Density. M.A. per Sq. Cm.	Overvoltage (Volts) on							
	Soft Graphite.	Au.	Cu.	Ag.	Platinised Pt.	Smooth Pt.	Spongy Ni.	Smooth Ni.
1	0.53	0.67	0.42	0.58	0.40	0.72	0.41	0.35
5	0.71	0.93	0.55	0.67	0.48	0.80	0.51	0.46
10	0.90	0.96	0.58	0.73	0.52	0.85	0.56	0.52
20	0.96	1.00	0.61	0.81	0.56	0.92	—	—
50	—	1.06	0.64	0.91	0.61	1.16	0.65	0.67
100	1.09	1.24	0.66	0.98	0.64	1.28	0.69	0.73
200	1.14	—	0.69	1.04	—	1.34	0.71	0.78
500	1.19	1.53	0.74	1.08	0.71	1.43	0.74	0.82
1000	1.24	1.63	0.79	1.13	0.77	1.49	0.76	0.85
1500	1.28	1.68	0.84	1.14	0.79	1.38	0.76	0.87

Many observations have been made with mercury electrodes. Heyrovský* worked with the mercury dropping kathode, and found that in a normal solution of hydrochloric acid, the current could be raised to 10^{-6} ampere at 1.2 volts without visible bubble evolution (Fig. 45). The hydrogen diffuses into the kathode and is unable to overcome both the capillary forces and the atmospheric pressure to form a bubble. The abnormally high overvoltage at the dropping kathode seems to be associated with the formation of a new mercury surface.

Herasymenko, Heyrovský and Taniakivský,† electrolysing mercurous salt solutions, found that both mercury electrodes were unpolarisable with small applied potential differences, the current increasing with the potential difference in accordance with Ohm's law until a certain critical value was reached, when the current attained a maximum, and then suddenly decreased to a much smaller value, which is known as the *diffusion current*. Increasing the potential still further, the diffusion current remained constant in value until a potential difference was applied large enough to deposit the hydrogen ions upon the kathode. The presence of an indifferent electrolyte, such as nitric acid, in small

* *Trans. Farad. Soc.*, 19, 785 (1923).† *Ibid.*, 25, 152 (1929).

quantities raised the value of the potential difference at which the maximum current occurred, whereas a large excess of the acid lowered it.

McAulay and Bowden,* using mixed electrolytes containing an acid and a metallic salt, found that the overvoltage at a mercury kathode was independent of the current density. Provided that the current carried by the hydrogen ions remained the same, the overvoltage was constant throughout a wide range of current

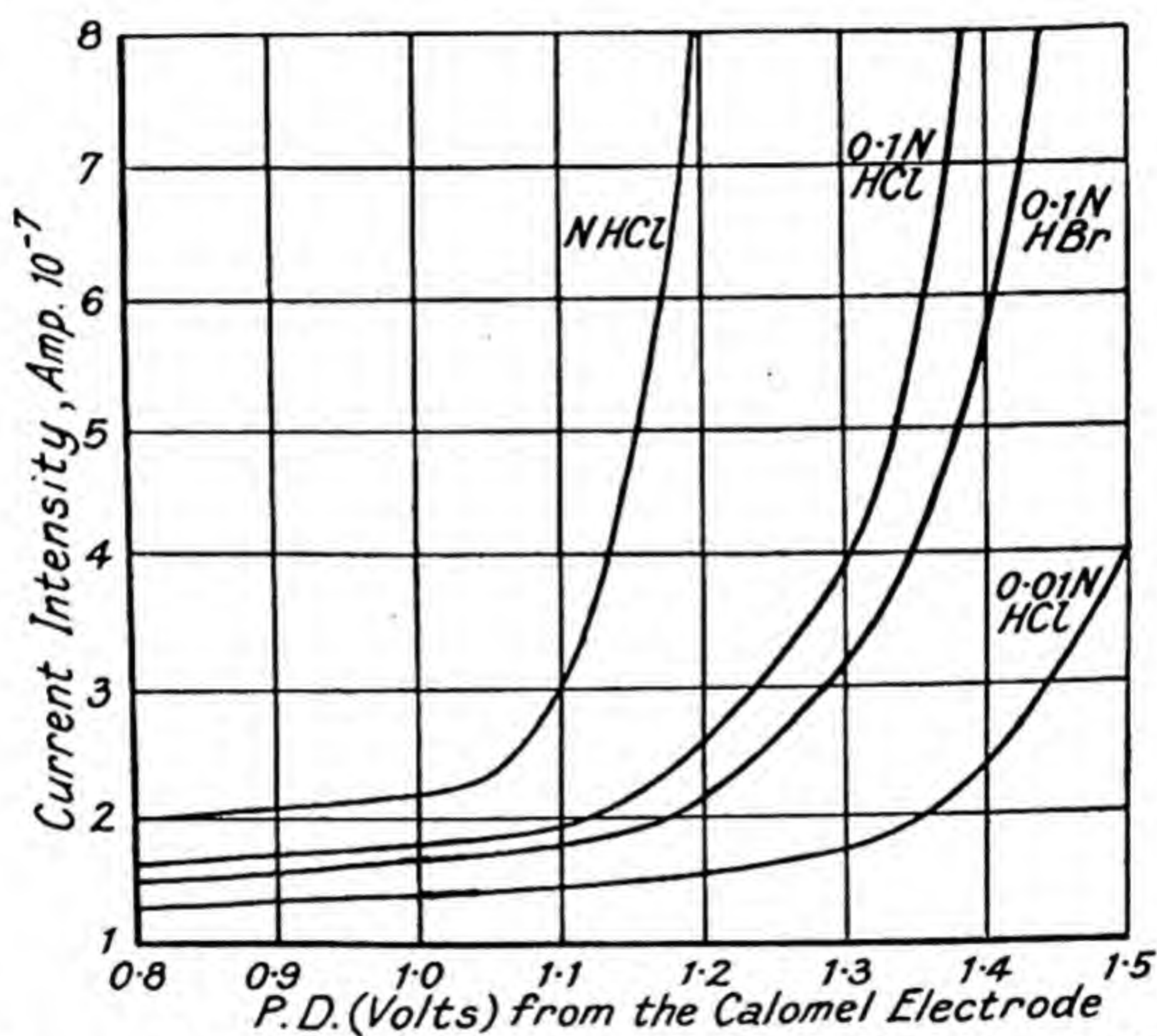


FIG. 45.—Hydrogen overvoltage at a mercury dropping electrode.

values. Once overvoltage had been established, both hydrogen and the metal were deposited at a high potential, characteristic of hydrogen, and independent of the reversible potential of the metal.

123. The variation of overvoltage.—With inactive metals the cathodic overvoltage is generally a linear function of the logarithm of the current density, and this relationship is particularly applicable to mercury and tantalum, although it does not hold at low current densities. The overvoltage on molybdenum and tungsten increases very slowly, while that on platinum, nickel and mercury rises rapidly with the current density. Rotating the kathode at high speed, 2000-6000 revolutions per minute, or

* *Phil. Mag.*, 1, 1282 (1926).

bubbling hydrogen, nitrogen, carbon dioxide, or oxygen over the electrode reduces the overvoltage at low, and to some extent, at high, current densities. The extent of the lowering depends upon the nature of the surface, being much larger, for example, with smooth tin than with rough copper. Overvoltage also increases with the time during which the metal is used continuously as a kathode.

Knobel * found that in all cases both the hydrogen and the oxygen overvoltages on spongy electrodes were smaller than on smooth electrodes. This may be due to the greater magnitude of the surface area, as well as to the changed nature of the surface.

On the whole we may represent the relationship between the cathodic overvoltage, E_{ov} , and the current density, i , by means of the formula,

$$E_{ov} = a + b \log i,$$

in which a and b are constants. This equation has been derived from theoretical considerations by Westrip.† It assumes that the current is proportional to the rate at which atomic hydrogen is removed in the form of molecules, and no allowance is made for the dispersal by diffusion into the electrolyte and the electrode. Taking this into account the formula becomes,

$$E_{ov} = a + b \log (i - k),$$

in which k is a third constant. Whilst, on the one hand, the overvoltage data for a lead kathode are in excellent agreement with this equation, it is found that the behaviour of a mercury kathode can be expressed by the simpler formula. Since, moreover, the simpler relation holds at very low current densities, it appears that very little hydrogen is removed from the mercury surface by diffusion. This is consistent with the fact that the maximum current which can pass without visible gas evolution is very much smaller with a mercury kathode than with one of lead.

The minimum potential difference, or that value which corresponds to the commencement of visible gas formation, should be, according to theory, independent of the nature of the electrolyte. Experiments made by Glasstone ‡ with a lead kathode show that this is the case, and that there is very little change when the hydrogen ion concentration is varied from 1 to 1×10^{-11} gram-ion per litre. On the other hand, results obtained by Sand and Weeks § with alkaline solutions and an antimony kathode indicate that the

* *Trans. Amer. Electroc. Soc.*, 47, 131 (1925).

† *Jour. Chem. Soc.*, 125, 1112 (1924).

‡ *Ibid.*, 125, 2414 (1924).

§ *Ibid.*, 125, 160 (1924).

overvoltage, measured by the commutator method with current densities sufficiently large to give reproducible results, is a linear function of the potential difference applied between a saturated calomel electrode and a hydrogen electrode, immersed in the electrolyte in question.

Trustworthy measurements of the influence of pressure on the overvoltage are not available, but concordant data * show that the overvoltage at a mercury kathode decreases with temperature by about two millivolts per degree C. The temperature coefficient at low current densities appears to be much greater for kathodes of low overvoltage value than for those of high overvoltage.† At low current densities the temperature influence is mainly determined by the temperature coefficient of the compensating processes, but at high current densities, when the electrode is covered by a gas film, the dominant factor is the influence of temperature on the ease with which bubbles of gas are liberated. Overvoltages and their temperature coefficients thus tend to become independent of the nature of the kathode at high current densities.

Experiments with binary alloy kathodes show that the overvoltage is independent of the proportions of the metals in the alloy, and is determined by that component which, in the pure state, has the smaller overvoltage.

MacInnes and Adler ‡ have shown that at very low current densities the overvoltage undergoes a periodic variation, corresponding to the formation, and release, of a gas bubble. At a small platinised-platinum kathode, with a current only sufficient to liberate a gas bubble every two minutes, they found that the overvoltage-time curve rose abruptly to a maximum after the bubble was released, then dropped suddenly to a minimum, after which it increased slowly to the point at which the next bubble of gas was released. Starting at the point at which the bubble separates, the voltage rises rapidly, since the layer of hydrogen on the electrode increases in thickness; but this layer soon becomes unstable, and the outer layers contract to form a bubble, the overvoltage falling to a figure corresponding to the thinner layer, *i.e.*, the minimum overvoltage. The layer then begins to grow again, but, in the presence of the already formed bubble, it gives up its outer molecules continuously, until the bubble leaves the electrode, after which the cycle is repeated.

* See Glasstone, *loc. cit.*; Bircher and Harkins, *Jour. Amer. Chem. Soc.*, **45**, 2897 (1923).

† See Rideal, *ibid.*, **42**, 94 (1920).

‡ *Jour. Amer. Chem. Soc.*, **41**, 194 (1919).

Sudden changes of overvoltage of considerable magnitude occur at some electrodes. They are attributed to a variation in the adsorbed gas layer, brought about by some change in the electrode surface. Newbery * found that at high current density the overvoltage at a mercury kathode suddenly decreased from nearly 2 volts to 0.55 volt, the excess back electromotive force, measured by the commutator method, at the same time falling to zero. In addition, the bubbles became exceedingly small in size. These facts can be explained on the gas-layer theory of overvoltage, which will be discussed later.

Colloids, dissolved in electrolytes, modify the overvoltage, generally raising it, although sometimes lowering it. Such substances are adsorbed by surfaces of solids, and therefore influence the adsorptive power of the electrode for the gas.

All investigators agree that oxygen overvoltages are more variable than those of hydrogen, and reproducible results are difficult to obtain. This may be due to the formation of actual oxide films, not always visible, on the anodes. In general, the anodic overvoltage is higher than the cathodic overvoltage on the same metal, under similar conditions, which is to be expected when we consider the greater affinity of metals for oxygen.

124. Transfer resistance.—As we have seen, much controversy exists as to the correct method of measuring overvoltage; whether it should be measured during the passage of a current through a cell, or whether the current should be interrupted by means of the rotating commutator, or similar device, before the electrode in question is connected to the potentiometer. Closely connected with this method of measurement is the question of the exact nature of the total opposition to the flow of a current from an electrolyte to an electrode. One school attributes the opposition to the back electromotive force, whereas the other suggests that a part of the opposition is due to a resistance. To investigate these points Newbery † traced out the complete time-potential curve of an electrode, when the existing current was made and broken, by means of a kathode ray oscillograph. The point brought out clearly in the resulting photographs is a large instantaneous potential drop when the main current is interrupted. This he attributes to an irreversible resistance effect between the kathode and the electrolyte, which he calls *transfer resistance*. Its value in some cases is as high as 100 ohms per square centimetre; it appears to be independent of the chemical constitution of the electrode, but is strongly affected by the mechanical condition of the

* *Jour. Chem. Soc.*, 121, 7 (1922). † *Proc. Roy. Soc., A*, 107, 486 (1925).

surface and, most of all, by the current density. So great is the influence of the last factor that at high current densities the transfer resistance at all electrodes is practically the same, and the effect may be looked upon as a physical, or mechanical, phenomenon.

The idea of a transfer resistance has not been generally accepted, and it is open to question whether the various figures, which are quoted by Newbery as representing the different states of overvoltage on a metal, really represent anything more than an alteration of the surface of the electrode, brought about by the solution of a small quantity of metal from the anode and its deposition on the kathode. Lattey* used a commutator in series with an oscillograph and examined the curve showing the relation between voltage and current. He found that the voltages could not be subdivided into overvoltages and transfer resistance effects. Very recently Newbery† has shown that the transfer resistance only occurs when gas is being liberated at an electrode, and becomes very small at high current densities. He concludes that this transfer resistance is solely the resistance of a gas film covering the electrode surface, and is not to be explained as due in part to a layer of partially exhausted electrolyte surrounding the electrode, as he had previously suggested. On the other hand, Heyrovský‡ has shown from observations on the overvoltage at a mercury dropping electrode that there is no indication of the formation of any kind of surface film.

Glasstone§ suggested that when overvoltage is measured by means of the direct method, a fall of potential, arising from the resistance of a thin film of electrolyte, is included; the higher the current density, the greater will be this additional potential. There certainly appears to be some kind of resistance at the surface of an electrode which affects the potential, as measured by the direct method. It may be due to a metal-gas-electrolyte system situated at the surface of the electrode; experiments indicate that this resistance is, in general, less than 4 ohms for an electrode of 1 sq. cm. exposed area.

125. Theories of hydrogen overvoltage.—Several theories have been advanced to account for overvoltage, some of which will now be considered. We know that if a metal is made the kathode in dilute sulphuric acid, even with a low cathodic potential, a considerable current passes for a very short time, followed by a slight residual current. Once the current has passed, the metal

* *Trans. Farad. Soc.*, 19, 838 (1924).

§ *Ibid.*, 810 (1924).

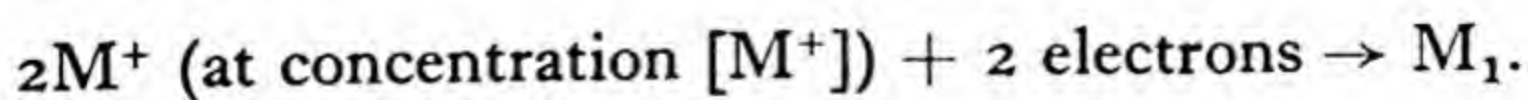
† *Proc. Roy. Soc., A*, 119, 686 (1928).

‡ *Trans. Farad. Soc.*, 19, 785 (1924).

electrode becomes, in effect, a hydrogen electrode, so that the hydrogen in some way must cover the metal surface, and it seems only natural to conclude that it is adsorbed at the surface. Rideal * suggested that the hydrogen ions were adsorbed at the electrode in order that they might be discharged. The discharged ions, *i.e.*, atoms, then unite to form molecules which are still adsorbed, but which diffuse at a definite rate into the electrolyte, or into any neighbouring gas bubble. Except at platinised platinum, and similar surfaces, this rate is equivalent to only a very small current density, and therefore at any ordinary current density, the ions must perform the work of desorbing the hydrogen molecules before they can discharge. This energy of desorption is supposed to be equivalent to the overvoltage.

If we consider an electrode of the substance M at concentration [M], dipping into an electrolyte containing the corresponding ion M^+ , at a concentration $[M^+]$, equilibrium is established when the potential difference between the electrode and the electrolyte is, say, π volts.† If, now, a current is passed through the system, the metal acting as kathode, a steady state is reached at which the concentration of the M^+ ions at the layer of electrolyte in immediate contact with the electrode is reduced to $[M^+]$ ', while the concentration of M in the effective surface layer of the electrode is increased to $[M]'$, the potential difference between the electrode and electrolyte now being π' , where $\pi' > \pi$, and $\pi' - \pi$ is the polarisation at the given current density. The maintenance of this steady state is evidently only possible if the ions M^+ are being continuously supplied to, and the metal M is continuously removed away from, the respective boundary layers. This may occur by a physical process such as diffusion, or by the occurrence of a chemical reaction. Thus, further reduction in the value of $[M^+]$ ' in the electrolyte boundary layer may be prevented by diffusion of M^+ ions from the region of higher concentration in the bulk of the electrolyte, or M^+ ions may be produced by some chemical reaction which can occur when the concentration of M^+ ions in any part of the electrolyte falls below a certain equilibrium value.

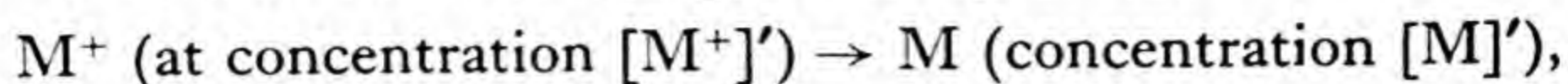
Suppose that the final result of these complex processes is the substance M_1 , existing under certain definite conditions, either within the electrode, or in some external system, so that



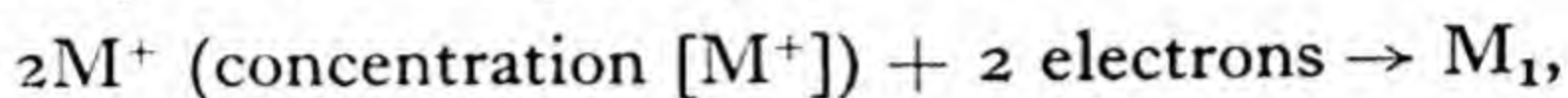
* *Jour. Amer. Chem. Soc.*, 42, 94 (1920).

† See Ellingham and Allmand, *Trans. Farad. Soc.*, 19, 762 (1923).

The increase in the free energy of the process,



which occurs at the free interface, electrolyte-electrode, may be only infinitesimally less than the electrical energy supplied to the system. The free energy of the final product M_1 will, however, be less than that of M —at concentration $[M]'$ —since the former is produced from the latter by a series of consecutive spontaneous processes, in all of which energy is dissipated into heat. Thus, the irreversibility of the complete process,



lies essentially in the irreversibility of the compensating processes, and the whole of the process arises from the relative slowness of these processes under the given conditions.

The only other way in which the polarisation phenomena can arise is by the hindrance of the electro-chemical process itself, such as if contact between the electrolyte and the electrode is partly prevented by a film, through which ions can only penetrate at certain parts. Finally, if this film, the substance of which is impenetrable to ions, is also non-porous and covers the electrode completely, thus reducing the free interface to zero, the only way in which the current can pass is by the discharge of ions at the film-electrolyte interface, the electrons passing across the film. The polarisation will now simply represent the potential difference necessary to overcome the ohmic resistance of the film.

In the discharge of the hydrogen ions at a metal electrode which has no chemical action on the electrolyte, it is very probable that the hydrogen is set free in the monatomic condition and then forms some kind of alloy with the electrode metal, such as exists in the case of palladium.

Whatever the mechanism which determines the velocity of the compensatory processes, it is evident that in cases where the processes are slow, a high hydrogen concentration may be produced in the electrode surface layers, before the production of hydrogen can keep pace with the rate of discharge of the hydrogen ions. Such electrode materials will have a high hydrogen overvoltage.

In opposition to these views is the theory that the polarisation is due essentially to the ohmic resistance of a complete gas film,* the thickness of which determines the overvoltage magnitude. In this case the cathodic overvoltage is the potential difference required to effect the passage of the electrons across the adsorbed

* See Knibbs, *Trans. Farad. Soc.* 19, 800 (1924).

film from the metal to the boundary of the electrolyte. It is possible that the ions themselves may have to pass through the gas layer.

The gas film on the electrode would grow until the thickness is such that the forces of adsorption on the outside layers are very weak. These layers will then become unstable and contract to form a bubble, which will continue to receive gas from the adsorbed layer as fast as the latter receives it by the discharge of ions, until the buoyancy of the bubble exceeds its attraction to the electrode. The attraction is largely determined by the electrical condition of the gas, since the latter, coming from an electrode, generally has a slight electrical charge. According to the gas-film theory, therefore, overvoltage is the fall of potential across the gas layer, adsorbed to the electrode surface, and the thickness of the layer is dependent upon the nature of the electrode surface, *i.e.*, its adsorptive power, the facility with which the bubbles are formed, and the current density.

126. Theories of oxygen overvoltage.—The case of oxygen overvoltage may be treated on similar lines. We know that if a potential difference be applied to platinum electrodes in dilute sulphuric acid, the potential of the anode increases, rapidly at first, bubbles of gas appearing when the potential exceeds 1.5 volts. After this stage the anode voltage continues to increase over a considerable range. Since liberation of oxygen-producing anions does not take place until the theoretical voltage—1.23 volts—has been considerably exceeded, it is obvious that the process taking place at the anode is not a reversible liberation of oxygen, but an irreversible process. The range of potential covered by this polarisation is nearly 3 volts, and therefore it is unlikely that the anodic polarisation is due to the formation of a film of oxygen, or of a physically adsorbed layer, as in the case of cathodic polarisation. Lorenz * and his school supported the oxide theory, and, more recently, Langmuir † found that activated platinum adsorbed oxygen at room temperature, forming a monomolecular layer of oxygen, which could not be driven off, either by heating or pumping. When the platinum was in contact with excess of oxygen the amount of oxygen adsorbed increased as the temperature was raised, but the action was irreversible. It is probable, therefore, that anodic polarisation is due to the formation of traces of oxide dissolved upon the surface of the electrode.

* *Zeits. Elektrochem.*, 15, 661 (1909).

† *Jour. Amer. Chem. Soc.*, 40, 1361 (1918).

Ellingham and Allmand * suggest that the case of oxygen over-voltage may be treated on lines similar to those used in discussing cathodic polarisation, although in the former case many compensating processes may be considered to operate.

127. Passivity.—If the product of the anode reaction is soluble, it will have but little influence upon the passage of a current from the electrode to the solution, although, so far as it accumulates at the anode surface, it will cause concentration polarisation, and thus retard somewhat the rate at which the anode goes into solution. If the product is insoluble, but porous or non-adherent, it will usually produce only a minor effect on the reaction, although the formation of any insoluble body will be unfavourable to diffusion and will thus tend to increase the concentration polarisation. If, however, the product is insoluble, and forms a film, closely adherent to the anodic surface, its presence will have a far-reaching effect. The product may prevent, more or less completely, the passage of further metal into the ionic state, whilst allowing other reactions to proceed, such as the production of oxygen gas. In some cases the protective action of the film may only be effective when the film becomes quite thick, and in such cases it is easy to study the material constituting the film, and to identify it with some known compound—lead peroxide, for example. In other cases the anodic product has so powerful a protective influence on the underlying metal, that the change is brought about when the film is apparently still of molecular thickness; the film is then invisible, and its presence must be inferred rather than proved directly. Such cases are included under the general term *passivity*.†

The point at which passivation occurs depends essentially upon the time throughout which electrolysis has proceeded, as well as upon the current density. Thus, if the latter is increased rapidly, the metal will remain active at higher current densities than would be possible if the increase were brought about more slowly. The production of the passive state is considerably influenced by the nature and concentration of the electrolyte. Ions having properties such as those possessed by OH^- , ClO_3^- , CrO_4^{--} favour the production of passivity, while H^+ , Cl^- and Br^- ions act in the reverse direction. Oxygen, dissolved in the electrolyte, also favours passivity.

There is a close connection between this anodic passivity and chemical passivity, which metals of the iron group show when

* *Trans. Farad. Soc.*, 19, 766 (1923).

† See Evans, *Trans. Farad. Soc.*, 19, 789 (1923).

dipped into solutions of oxidising agents, such as nitric acid, or chromic acid of suitable concentrations.* Chemical passivation involves an increase in the potential of the metal with reference to the solution, and after the transition the metal is practically insoluble in solutions, whereas previously it readily corroded.

Passivity phenomena of a similar kind have been observed in the anodic behaviour of various metals besides iron, cobalt and nickel. Thus gold dissolves anodically in HAuCl_4 solutions as Au^{++} ions up to a certain value of the current density, but above this value the gold becomes passive, and chlorine is evolved in the main process. Chromium dissolves anodically in an iodide solution up to moderate current densities; at a certain point metal solution gives place to iodine deposition. With chromium anodes in most electrolytes, however, the reaction is not the discharge of anions, but solution of the metal with a higher valency. Thus Hittorf † found that at ordinary temperatures chromium in dilute hydrochloric acid or sulphuric acid would scarcely dissolve as Cr^{++} or Cr^{+++} , but at higher temperatures the metal dissolved readily as Cr^{+++++} , giving CrO_4^{--} .

There appear to be degrees of passivity. Metallic specimens are met with from time to time in a state which is best described as partially passive. If the passivity is due to the presence of adherent oxygen atoms upon the metallic surface, it is easy to see that the passivity will increase, and the potential will rise, as the surface concentration of oxygen increases, or, as the concentration of oxidising agents in the solution increases.

It is possible that the transition to the passive state occurs as the result of the formation of a film of some definite oxide of the metal. The onset of passivity may be regarded as due to the production of a film which causes a transfer resistance. An oxygen film might act in this way, but the existence of films of this kind, of sufficient thickness to offer an appreciable ohmic resistance, is less likely than in the case of oxygen overvoltage, since the transition to the passive state usually sets in at a potential below that calculated for a reversible oxygen electrode in the given solution. It may be concluded therefore that anode metal solution is practically prevented when a definite oxygen concentration at the electrode surface is produced. As soon as this state of affairs is reached, the potential rises until another electrochemical process can maintain the current density; in the passivation of the iron group of metals this process will be oxygen evolution. When the transition has occurred, the current density

* See Ellingham and Allmand, *loc. cit.*

† *Zeits. Elektroc.*, 4, 482 (1898); 7, 168 (1900).

may be reduced considerably, and all the current is used in the production of oxygen. Even at low current densities this can proceed rapidly enough to maintain an oxygen concentration in the electrode surface, sufficient to protect the metal. A decrease in temperature favours passivation, but, on the other hand, a superposed alternating current tends to prevent the accumulation of oxygen at the surface, and this favours the maintenance of the active state.

Schulze * has found that certain metals, used as anodes in the electrolysis of dilute sulphuric acid and of other solutions containing oxygen, become coated with a film which effectively stops the current. This *valve* action is particularly strong in the cases of aluminium, tantalum and tungsten, and seems to be due to the formation of a very thin layer of gas of high resistance, and a thicker porous layer of metallic oxide, the pores of which are filled with electrolyte and gas. The whole may be compared with a condenser, and since the capacity and resistance of the formed anode are both very high, the electrical charge accumulated cannot disappear in a moment. The resistance of the oxide layer seems to be small in comparison with that of the gas layer, and the ohmic resistances are by no means constant. The film formation becomes more and more difficult as the temperature rises to 100° C.

Smits † disagrees with Schulze's view that the passivity of aluminium during anodic polarisation is due to the formation of a layer of alumina of high resistance. He considers that, although a coating of oxide, or basic salt, is formed at higher potentials, this explanation cannot be reconciled with the fact that at lower potentials, where passivity is also shown, the aluminium electrode remains bright, and that when the current is reversed the resistance disappears. Smits found that on anodic polarisation, the potential of the metal became so strongly positive, that the potential difference necessary for the separation of the oxygen was reached at very low current densities. He considers that this change of potential is the primary phenomenon, and the separation of the oxygen, and subsequent oxide formation, is a secondary action. The increase of the aluminium potential is explained by the withdrawal of electrons from the metal, this withdrawal being followed immediately by the aluminium going into solution. The formation of the aluminium ions within the solid metal proceeds slowly. Through the withdrawal of electrons and ions the metal surface

* *Ann. d. Phys.*, 22, 543 (1907), and numerous other papers noted in the bibliography.

† *K. Akad. Amsterdam, Proc.* 22, 876 (1920).

passes into a state which resembles a metalloid, and possesses an exceedingly small electrical conductivity.

This valve action may be used to rectify alternating currents, and Newman * has shown that if these currents are of frequency 60 per second, and the applied voltage not too high, say 100 volts or less, rectification is practically complete one minute after starting the alternating current, even when the anode has not been previously formed.

128. Alternating current electrolysis.—The subject of alternating current electrolysis has been investigated by many workers.† Most of them dealt with the passage of alternating current through solutions of cyanides and chlorides, and they were chiefly concerned with the question of the solution of the electrodes, and the chemical changes occurring in the electrolytes. Ruer ‡ used platinum electrodes in dilute sulphuric acid. He found that the platinum was not dissolved by the alternating current alone, but that it was dissolved when the electrodes, between which the alternating current passed, were subjected to anodic polarisation. This result was contested by Brochet and Petit,§ who maintained that the solution of the platinum is due to the current density variation, and not to any specific action of the alternating current.

Marsh || found that with alternating current electrolysis the rate of gas evolution was by no means constant, but fell off rapidly with time, and finally ceased altogether. With platinum foil in dilute sulphuric acid, the curves showing the relation between the volume of gas given off and the time, for different current frequencies, bear a striking resemblance to the saturation curves in radioactivity. For equal current density, the total volume of the gas liberated at an electrode is proportional to its area, the frequency being constant throughout.

The various effects are brought about by two actions : (a) the changes occurring at, and inside, the electrode, (b), the changes taking place in the electrolyte. We can imagine that some of the gas liberated in any single half period is kept at the electrode, and then attacked by the gas liberated in the succeeding half period, water being reformed. Hence the total volume of gas actually liberated is considerably less than the theoretical value. Now

* *Phil. Mag.*, 49, 1029 (1925).

† See Le Blanc and Schick, *Zeits. Phys. Chem.*, 46, 213 (1903) ; Maneuvrier and Chappuis, *Comptes Rendus*, 107, 31 (1889).

‡ *Zeits. Elektroc.*, 9, 235 (1903).

§ *Ann. Chim. Phys.*, 3, 453 (1904).

|| *Proc. Roy. Soc., A*, 97, 124 (1920).

hydrogen is easily absorbed by platinum, and hence of the hydrogen produced in one half period at one electrode, some will escape, and some will be absorbed by the electrode. Of the oxygen produced at this electrode during the succeeding half period, some will escape, some will attack the hydrogen in the electrode, reforming water, and some will undoubtedly react with the electrolyte. As a variation of the above process, it might be supposed that the portion of the hydrogen which remains at the electrode does not stay at the surface to be wholly, and entirely, removed by the oxygen at the succeeding half period, but diffuses into the electrode in accordance with the ordinary laws of diffusion. The hydrogen of the succeeding period is not able to diffuse as rapidly into the electrode owing to the gas already present in the electrode. Hence, more and more oxygen is removed by recombination. According to this view, it would appear that oxygen is in excess in the evolved gases, but careful tests by Marsh showed that oxygen was, if anything, in deficit.

On the other hand, we may conceive the processes as chemical changes, occurring at the electrodes, during the passage of the alternating current. The electrode may become oxidised, the resulting oxide being reduced to some lower oxide, or to the metal itself, by the hydrogen formed during the next half cycle. Such oxidation and reduction would alter the constitution of the surface, making it more porous in nature, thus exposing a greater area to the subsequent oxidising and reducing actions. Results seem to support the view that in the case of gold and nickel, oxidation occurs during the process of electrolysis.

It has been found * that there are undervoltages on platinum, tungsten and molybdenum when a direct current is passed at the same time as an alternating current, and in all cases, except at a smooth or rough copper kathode, the overvoltage is lowered. These general effects are such as would be expected if the hydrogen is oxidised, presumably while still in the atomic state.

Brown † has shown that if alternating current of suitable strength is sent through a zinc-sulphuric acid-carbon cell, itself fitted up so as to discharge through a low resistance circuit, the polarisation of the cell is destroyed, and its current output materially increased. He found this effect was greater if the cell had a small zinc electrode and a large carbon electrode, than if the electrodes were of the reverse size. From these results he concluded that, while the carbon electrode surface only affects the results in so far as it determines the cell resistance, the alternat-

* See Harkins and Adams, *Jour. Phys. Chem.*, 29, 205 (1925).

† *Proc. Roy. Soc., A*, 90, 26 (1914).

ing current, in some manner, increases the velocity of the SO_4^{--} ions in the neighbourhood of, and towards, the zinc anode, the latter being more rapidly dissolved.

Allmand and Puri * found that a superposed alternating current had the greater effect upon the carbon electrode, and this result was supported by electrode potential measurements. To investigate the effects produced at a single electrode, without disturbing directly the general working of the cell, auxiliary electrodes were introduced which served to lead the alternating current to the particular cell electrode under study, as shown in Fig. 46. The arrangement shown in Fig. 46 (a) was used when investigating the carbon electrode, and that in Fig. 46 (b) when the zinc electrode was tested. The applied alternating voltage was adjusted by

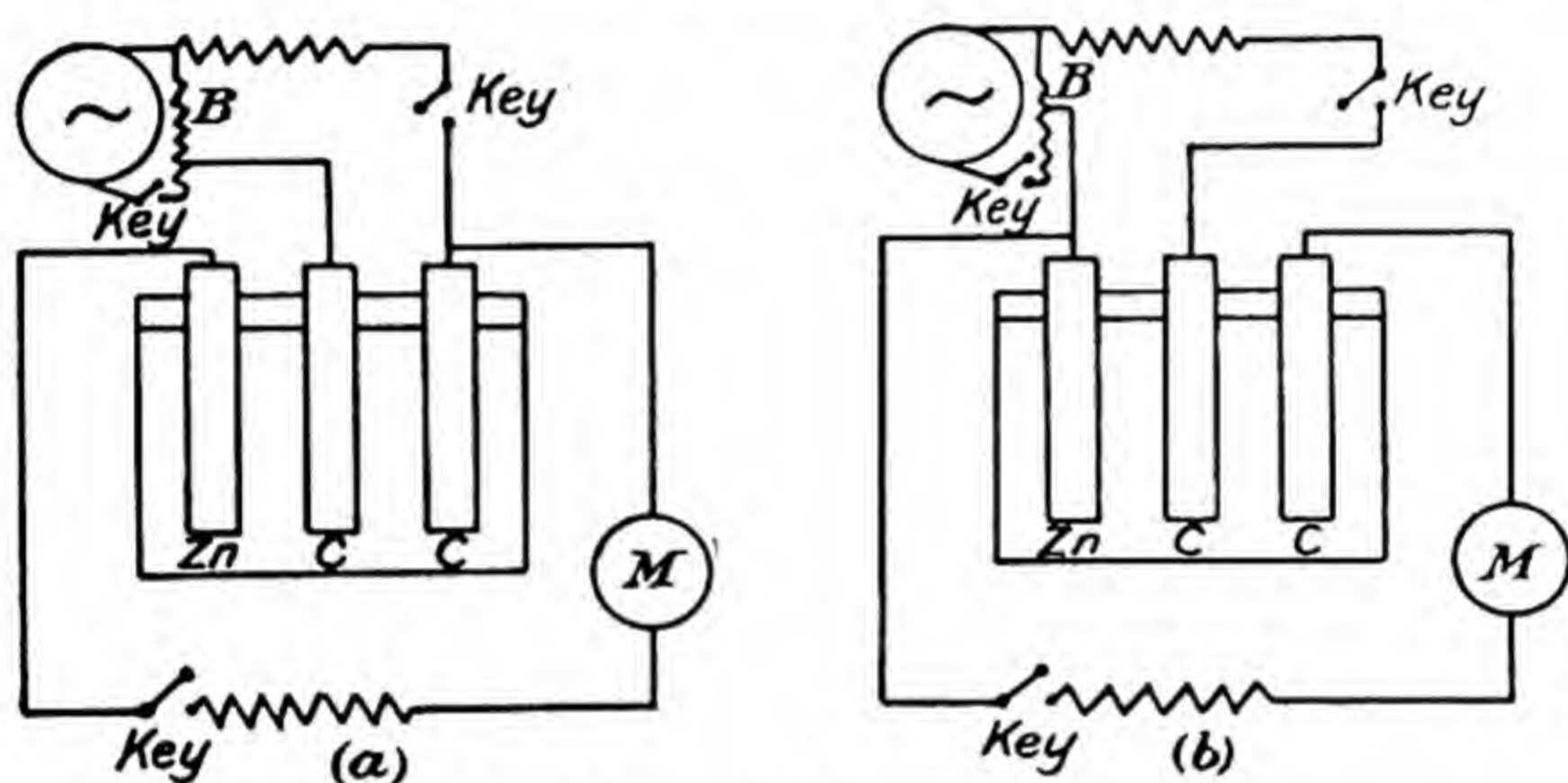


FIG. 46.—Alternating current electrolysis.

means of the resistance, B , and the ammeter, M , measured the current.

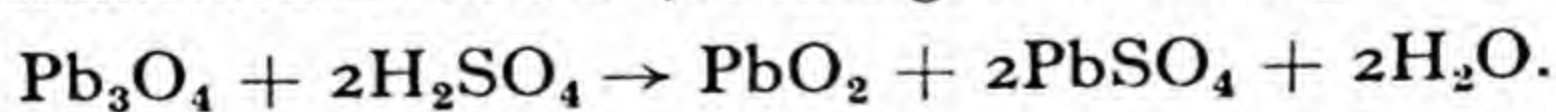
The chief effect of the alternating current was confined to the carbon electrodes, the lower frequencies producing the greater effects, and the difference at the two electrodes being more pronounced with small current values. At the zinc electrode the change in potential was in the direction of a depolarisation, and this indicated that since the electrode behaves irreversibly in the absence of an alternating current, the effect of the latter is to cause a dissolving of the zinc anode to act like a more electro-positive metal.

In general there was a marked depolarisation of hydrogen ion discharge, this effect increasing with the strength of the alternating current. The influence of the frequency was most marked, the polarisation being considerably lowered as the periodicity increased.

* *Proc. Roy. Soc., A*, 107, 126 (1925).

It appears that the oxygen discharged during the anodic pulse of the alternating current, by combining with, or displacing, the active hydrogen at the kathode, lowered the electrolytic solution pressure of the kathodic metal. Expressed formally, the results correspond to an increase in the electrolytic solution pressure of the metal, or to a decrease in the zinc ion concentration in the electrolyte at the electrode surface. The direct current polarisation would explain, qualitatively, the phenomenon at the kathode, but not that at the anode.

129. Accumulators.—Any reversible cell can be used as an accumulator, but the simplest, and most usual type, consists of two lead plates immersed in dilute sulphuric acid. If an electric current is passed between these plates, the anode will become oxidised at the surface to lead dioxide, while at the kathode hydrogen gas is evolved, the lead remaining in its original condition. As long as the metallic lead of the anode is in contact with the solution, hydrogen is evolved at the kathode under a total electromotive force of 0.5 volt, approximately, but eventually, when the lead dioxide has been formed, the force necessary for the generation of hydrogen rises to about 2.2 volts. After this forming process has continued for some time, the cell is in a condition to give a current in the reverse direction, during which lead sulphate is formed at both electrodes until they become practically identical in constitution. By repeatedly reversing the direction of the current, the lead dioxide permeates deeper and deeper into the positive plate, and the lead sulphate at the kathode is reduced to spongy lead. This condition is also brought about by continual charging and discharging. The alternate charging and discharging, which is necessary to form the accumulator plates, is a lengthy process, and the whole preliminary forming can be greatly accelerated if the plates are packed, or coated, with red lead. This, on being immersed in the acid, is changed according to the reaction :



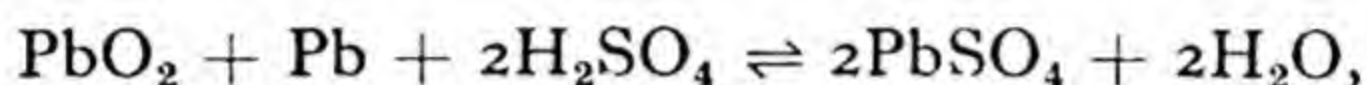
The red lead forms a kind of cement with the sulphuric acid, and assumes a solid consistency. Usually the cells are made up with Planté formed anodes and pasted kathodes, so that they withstand heavy discharge without danger of the positive plates disintegrating. An objection to the formed plates is that they do not hold well together, and cannot withstand very heavy currents, which, being accompanied by chemical processes involving changes of volume, cause disintegration of the positive plate.

The formation of the plates may be assisted by adding a

catalyst to the sulphuric acid, such as a perchlorate, or a chlorate. In this case, if the ratio of the SO_4^{--} anion concentration to that of the added anion is not too great, the lead sulphate is formed at a very short distance away from the plate, and not actually on the plate.

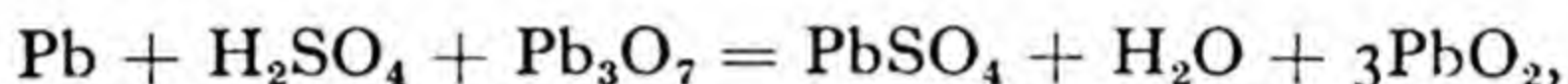
When fully charged the acid has a density equal to 1.205-1.215 grams per c.c., and must be free from certain impurities, such as chlorine, and foreign metals, since, if these are present, the lead plates are violently attacked. Thus, the water used in filling up the cell to replace that lost by evaporation should be entirely free from chlorides.

The main chemical action of a fully formed accumulator may be expressed by means of the equation,

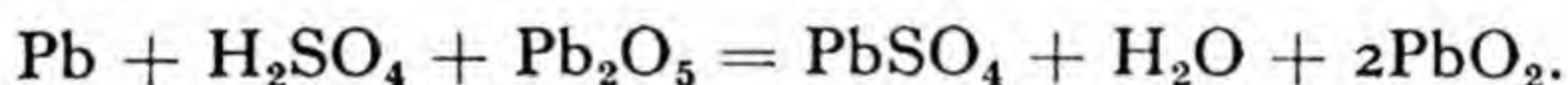


the discharge being represented when read from left to right and the charging when read from right to left.

Féry * suggested that the reaction during discharge should be expressed thus,

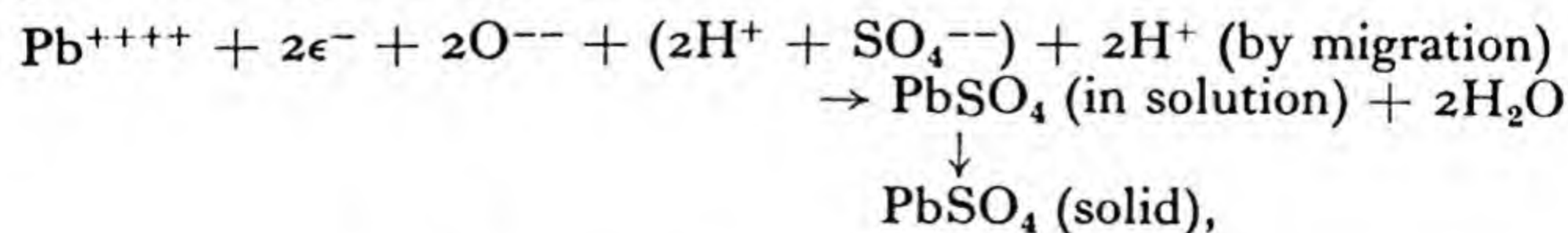


or, possibly,



From these equations it follows that only one mole of sulphuric acid per two faradays of electricity is used, whereas the more generally recognised reaction involves two moles of acid per two faradays. Knobel † carried out an investigation with a view to determining whether the reactions suggested by Féry, or those of the usual double sulphate theory, are correct. Experiment shows that the amount of acid used varied with the rate of discharge, but at low rates two moles per two faradays were required. It thus appears that Féry's theory is not supported.

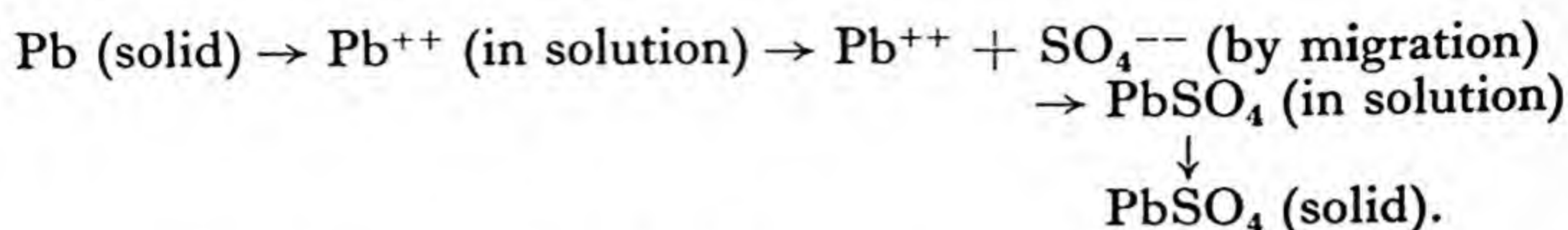
During discharge the anode, or positive plate, becomes covered with lead sulphate according to the reaction, which may be represented by the equation,



* *Bull. Soc. Chim.*, 25, 223 (1919).

† *Trans. Amer. Electrochem. Soc.*, 43, 99 (1923).

where ϵ represents an electron. The action at the kathode may be represented by the equation,



According to Liebenoff,* when an accumulator is being charged, the Pb^{++} ions are deposited primarily upon the kathode, and PbO_2^{--} ions upon the anode. Although, on account of the small solubility of lead sulphate, very few of these ionic species are present in solution, they are continuously replaced from the lead sulphate on the electrode. It is only when the lead sulphate has disappeared that the sulphuric acid is electrolysed, hydrogen appearing at the kathode, and oxygen at the anode.

When bodies are formed electrolytically, it is conceivable that they may differ somewhat from apparently the same bodies, formed by ordinary chemical means, but the measurement of the electromotive force affords a method of detecting differences. It is found that a plate composed of chemically prepared PbO_2 gives the same electromotive force as that observed with the positive plate of a lead cell, formed in the ordinary way. Analysis of the active material, at various stages of the charge and discharge, has proved that PbO_2 is the active material on the positive plate.

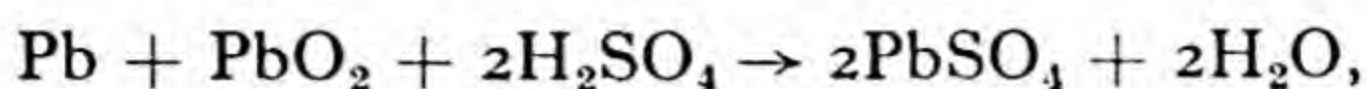
It will be realised that if the above equations are true, and involve ionic, as distinct from ordinary chemical changes, the various bodies formed, or decomposed, must be formed, or decomposed, in proportion to the quantity of electricity which passes on charge, or discharge. As stated previously, this condition is satisfied as regards the sulphuric acid, but the lead sulphate has been the subject of much discussion. The formation of the sulphate on the negative plate has been found, on analysis, to agree satisfactorily with that required by theory, but as regards the positive plate, the agreement is not so good. This is to be expected if the change from a reduced oxide to sulphate is a secondary reaction.

If the accumulator system is reversible, we may apply the Gibbs-Helmholtz relation,

$$\psi = E + T \frac{d\psi}{dT}.$$

* *Zeits. Elektrochem.*, 2, 420 (1895).

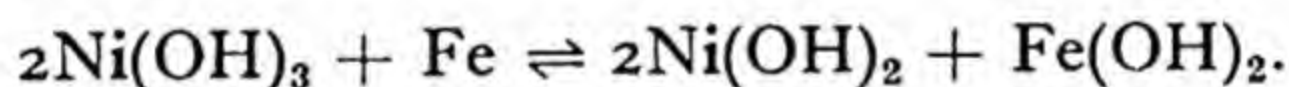
According to the measurements of Thomsen * the reaction,



evolves 43,500 calories for every gram-equivalent of lead which is transformed. Assuming that all of this energy is available, the electromotive force of the cell is 1.88 volts, a value which agrees with that experimentally observed for cells containing a weak acid. Hence the temperature coefficient of this type of cell must be low. This has been confirmed experimentally by Streintz † who found that with acid of density 1.153 grams per c.c., the electromotive force of the accumulator increased by 32×10^{-5} volt per degree C. rise of temperature. He also measured the reversible heating effect experimentally, and found it to be 17,400 joules per faraday at 273° absolute, whereas the calculated value is 18,200 joules per faraday.

The electromotive force of the accumulator increases with the acid strength, since part of the available energy of the reaction is due to the dilution of the residual acid by the formed water.

In another type of accumulator, known as the *alkaline accumulator*, the electrolyte is potassium hydroxide solution, and the most favourable results are obtained when iron and nickel peroxide form the active plates. The reactions that take place can be represented by the equation,



The electrolyte is apparently unaffected, its density change during the operation of the cell being very small. In the plates themselves changes of concentration of the electrolyte occur according to the rate of charge or discharge. A comparatively small volume of electrolyte is required owing to the fact that it does not enter into any chemical action, or combination with the active materials, but merely acts as a conductor for the hydroxyl ion from plate to plate.

These alkaline accumulators have excellent keeping qualities, the loss of charge over a period of three months, on open circuit, being unimportant, but at low temperatures their internal resistance is high, and consequently the capacity is much impaired. The average working voltage is 1.2 volts.

* *Wied. Ann.*, 11, 246 (1880).

† *Ibid.*, 46, 454 (1892).

BIBLIOGRAPHY.

- Allen, Trans. Farad. Soc., 9, 247 (1914).
 Aten, Proc. Amst. Acad., 19, 653, 768 (1917).
 Bairsto and Mercer, Trans. Farad. Soc., 7, 1 (1911).
 Bowden, *ibid.*, 24, 473 (1928).
 Brockman, Trans. Amer. Electrochem. Soc., 47, 245 (1925).
 Brönsted, Zeits. phys. Chem., 65, 84 (1909).
 Byers and Langdon, Jour. Amer. Chem. Soc., 36, 2004 (1914).
 Byrne, Trans. Farad. Soc., 23, 661 (1927).
 Cottrell, Zeits. phys. Chem., 42, 385 (1903).
 Dunnill, Jour. Chem. Soc., 119, 1081 (1921).
 Eggert, Zeits. Elektrochem., 33, 94 (1927).
 Evans, Trans. Farad. Soc., 9, 310 (1913); 18, 1 (1922); Jour. Chem. Soc., 1020 (1927).
 Foerster, Zeits. phys. Chem., 69, 236 (1909).
 Frendenhagen, *ibid.*, 43, 1 (1903).
 Glasstone and Symes, Trans. Farad. Soc., 23, 213 (1927).
 Grant, Trans. Farad. Soc., 24, 367 (1928).
 Grube, Zeits. Elektrochem., 15, 769 (1909); 16, 621 (1910); 33, 389 (1927).
 Grube and Dulk, Zeits. Elektrochem., 24, 237 (1918).
 Guthe, Phys. Rev., 15, 327 (1902).
 Heathcote, Jour. Soc. Chem. Ind., 26, 902 (1907).
 Hedges, Jour. Chem. Soc., 969 (1928).
 Herasymenko, Zeits. Elektrochem., 34, 129 (1928).
 Hevesy and Slade, *ibid.*, 18, 1001 (1912).
 Hitchcock, Trans. Amer. Electrochem. Soc., 25, 415 (1914).
 Lewis, Zeits. phys. Chem., 55, 465 (1906).
 Liebreich and Wiederholt, Zeits. Elektrochem., 34, 28 (1928).
 Lobry de Bruyn, Rec. Trav. Chem., 40, 30 (1921).
 MacInnes, Jour. Amer. Chem. Soc., 42, 2233 (1920).
 Müller, Zeits. phys. Chem., 65, 226 (1909).
 Müller, Zeits. Elektrochem., 33, 401 (1927).
 Nernst, Zeits. phys. Chem., 47, 52 (1904); Zeits. Elektrochem., 11, 835 (1905).
 Nernst and Merriam, Zeits. phys. Chem., 53, 235 (1905).
 Ralston, Trans. Amer. Electrochem. Soc., 47, 193 (1925).
 Rathert, Zeits. phys. Chem., 86, 569 (1914).
 Reichinstein, Zeits. Elektrochem., 18, 850 (1912).
 Rideal, Trans. Farad. Soc., 9, 281 (1914).
 Schmidt, *ibid.*, 9, 257 (1914).
 Schoch, Amer. Chem. Jour., 41, 209 (1909).
 Schoch and Randolph, Jour. Phys. Chem., 14, 719 (1910).
 Schulze, Ann. d. Phys., 22, 555 (1907); 23, 226 (1907); 24, 43 (1907); 25, 775 (1908); 26, 372 (1908); 65, 223 (1921); Zeits. Elektrochem., 14, 303 (1908).
 Senter, Trans. Farad. Soc., 9, 203 (1914).
 Smits, Proc. Amst. Acad., 22, 876 (1920).
 Spitzer, Zeits. Elektrochem., 11, 345 (1905).
 Stapenhorst, Zeits. phys. Chem., 92, 238 (1917).
 Trans. Farad. Soc., 19, 667 (1924).
 Walter, Electrician, 71, 1057 (1913).
 Watts, Trans. Amer. Electrochem. Soc., 19, 103 (1911).

CHAPTER IX.

THE MEASUREMENT OF ELECTROLYTIC RESISTANCE.

130. Introduction.—The experimental determination of electrolytic resistance is complicated by the existence of polarisation phenomena, and the ordinary Wheatstone bridge method, employing steady currents, cannot be used to measure the resistance, since, in general, we are not justified in assuming that the current is simply proportional to the applied potential difference between the electrodes. The back electromotive force of polarisation, which arises when the electrical current is passed through the electrolyte, opposes the main potential difference, and if the latter happens to be small, the ratio of applied potential difference to the resulting current may be extremely high.

Consider an electrolytic solution, subjected to an alternating electromotive force, applied between two electrodes, immersed in the solution, then, as shown, by Kohlrausch,*

$$\mathbf{E}_0 \sin pt = Ri + P \int i dt, \quad . \quad . \quad . \quad (144)$$

where \mathbf{E}_0 is the maximum value of the applied electromotive force, R , the resistance of the electrolyte, i , the current, P , the polarisation and $\frac{2\pi}{p}$, the period of the alternating current.

Differentiating this equation, we have

$$\mathbf{E}_0 p \cos pt = R \frac{di}{dt} + Pi,$$

whence
$$i = \frac{\mathbf{E}_0}{R \left(1 + \frac{P^2}{p^2 R^2} \right)^{\frac{1}{2}}} \sin (pt + \theta), \quad . \quad (145)$$

in which
$$\tan \theta = \frac{P}{pR},$$

* Kohlrausch and Holborn, "Leitvermögen der Elektrolyte."

and the effective resistance is given by

$$R\left(1 + \frac{P^2}{p^2 R^2}\right)^{\frac{1}{2}}.$$

The resulting current is not in phase with the applied electromotive force, but if P is negligible compared with pR , then $\theta = 0$,

and
$$i = \frac{E_0}{R} \sin pt.$$

Hence the effective resistance becomes the true resistance of the electrolyte, and may be measured by the Wheatstone bridge method, if a suitable type of galvanometer, or indicating instrument, is used in the bridge. If, therefore, the quantity of electricity passed through the solution is small, and the electrode surfaces large, so that the polarisation is small, and since, in addition, the polarisation effects are non-cumulative with alternating currents, electrolytic resistances can be measured by means of the same principle as that employed in the determination of metal resistance. Even if the imposed electromotive force is not harmonic in character, but only alternating in direction, provided that the quantities of electricity which pass during the alternations are equal, the polarisation effects are still more or less annulled. It will be observed that they depend upon the frequency of alternation, p , and for a given value of p they vary with $\frac{P}{R}$, so that the higher the frequency, the less important these effects become. Since P has been shown to be inversely proportional to the capacity at the electrode-liquid interfaces, **section (115)**, polarisation decreases as the electrode areas increase, especially if the electrolytic resistance is high. The effective areas of platinum electrodes may be augmented by platinisation.

On the other hand, polarisation effects become serious if the value of $\frac{P}{R}$ is large, hence a type of cell in which $\frac{P}{R}$ is small must be used if an accurate determination of R is required. Assuming that the polarisation, P , is exactly equivalent to a capacity, $\frac{1}{c}$, its effect may be counterbalanced by inserting a self-inductance of value L in the same arm of the bridge. In this case the potential difference applied across the end of a bridge arm, containing an electrolytic solution and this self-inductance, is given by the equation,

$$E_0 \sin pt = Ri + \frac{1}{c} \int i dt + L \frac{di}{dt},$$

from which by integration,

$$i = \frac{E_0}{R \left[1 + \frac{\left(\frac{1}{c} - Lp^2 \right)^2}{p^2 R^2} \right]^{\frac{1}{2}}} \sin (pt + \theta),$$

where

$$\theta = \tan^{-1} \frac{\frac{1}{c} - Lp^2}{pR},$$

$\frac{1}{c}$ being equal to P . Hence the effect of the self-inductance is opposed to that of the polarisation, and by choosing suitable values, it is possible to make $P - Lp^2 = 0$. Then the capacity effect of the electrolytic cell in a bridge arm is compensated for, and both R , the true resistance, and P , the polarisation capacity effect, may be calculated, if p and L are known.

We may write equation (145) in the form,

$$i = i_0 \sin (pt + \theta),$$

where

$$i_0 = \frac{E_0}{R \left(1 + \frac{P^2}{p^2 R^2} \right)^{\frac{1}{2}}},$$

and is the maximum value of the current. Hence the back electromotive force E_p , being equal to $P \int i dt$, is given by

$$E_p = - \frac{Pi_0}{p} \cos (pt + \theta),$$

and therefore differs in phase from the current by 90° .

Smith and Moss* have pointed out that most, if not all, electrolytic condensers are leaky, the leakage increasing with the degree of polarisation at the electrode. However small the potential difference applied to an electrolytic cell may be, there is always a residual current, so there must be a continuous flow of electricity through the circuit. Thus $\frac{dE_p}{dt}$ is not equal to

$P \frac{dQ}{dt}$, where Q is the electrical charge on the condenser plate, but

$$\frac{dE_p}{dt} = P \left(\frac{dQ}{dt} - \frac{dQ'}{dt} \right) = P(i - i_L),$$

* *Proc. Phys. Soc.*, 25, 133 (1912).

where $\frac{dQ'}{dt}$ is the rate at which the charge leaks from the condenser, i , the current passing through the cell, and i_L , the leakage current. If we assume that the latter is proportional to the polarisation, then,

$$\frac{dE_p}{dt} + PbE_p = Pi_0 \sin pt,$$

b being a constant. Hence,

$$E_p = - \frac{Pi_0}{p \left(1 + \frac{P^2 b^2}{p^2} \right)^{\frac{1}{2}}} \cos (pt + \phi),$$

or
$$E_p = - \frac{P'i_0}{p} \cos (pt + \phi)$$

where
$$\tan \phi = \frac{Pb}{p} \text{ and } P' = \frac{P}{\left(1 + \frac{P^2 b^2}{p^2} \right)^{\frac{1}{2}}}.$$

In the absence of leakage,

$$E_p = - \frac{Pi_0}{p} \cos pt,$$

so that leakage decreases the value of the back electromotive force, and ϕ represents the phase difference of this back E.M.F. in the two cases, with and without leakage. Hence, assuming leakage across the electrolytic condensers, and equating the applied potential difference to the sum of the various potential differences existing in an electrolytic cell, we have, on writing

$-\frac{P'}{p}i_0 \cos (pt + \phi)$ for $P \int idt$ —the back electromotive force—that,

$$E_0 \sin pt = i_0 \left\{ \left(R + \frac{P'}{p} \sin \phi \right) \sin pt + \left(Lp - \frac{P'}{p} \cos \phi \right) \cos pt \right\}.$$

Thus E and i , the instantaneous values of the applied electromotive force and the current, will be in the same phase, *i.e.*, their ratio will be the same at any instant, if

$$Lp = \frac{P'}{p} \cos \phi,$$

and the value of the ratio $\frac{E_0}{i_0}$, the effective resistance, is given by

$$R + \frac{P'}{p} \sin \phi.$$

Hence, in general, the effective resistance is not constant, but is a function of p , the frequency of alternation.

This leakage effect is only one of several complex phenomena that may take place between polarised electrodes and the surrounding solution.

131. Experimental determination of electrolytic resistance.—In general, the methods of measuring the resistance of electrolytes may be divided into two classes :—

(a) Those in which the effects of polarisation are avoided, and

(b) Those in which polarisation is reduced to a minimum.

(a) *Methods not involving polarisation.*—The detrimental effects of polarisation may be avoided by inserting a second electrolytic cell, similar in all respects to the first one, but containing a different length of the solution, in the conjugate arm of a Wheatstone bridge. A balance with direct currents for a particular length of the solution in one cell is obtained, and then the distance between the electrodes is diminished by a measured amount, the known resistance in this arm in series with the electrolyte being increased so as to restore the balance. A conceivable source of error arises in consequence of moving the electrode, since a possible alteration in the polarisation may occur. Tollinger's results * with this method were about 0.6 per cent. lower, on the average, than those obtained with the alternating current method. Elsas † used a long trough, of known cross-section, with two fixed non-polarisable electrodes, such as copper plates in copper sulphate solution, at the ends and one movable electrode between them. A resistance, in series with the shorter liquid column, was adjusted to balance the bridge.

Smith and Moss ‡ worked with auxiliary, or potential electrodes, the potential drop being measured by an electrostatic voltmeter of negligible capacity. The apparatus which they used is shown in Fig 47. Alternating currents, measured by means of the ammeter, A , were passed through the electrolytic solution by way of the main electrodes, p and q , and the resulting potential difference between the ends of the tube containing the electrolyte was measured by means of the electrostatic voltmeter, V , and the auxiliary electrodes, p' , q' . The ratio of the voltmeter and ammeter readings gave the resistance. For direct currents it is necessary to use a voltmeter of high resistance, compared with

* *Wied. Ann.*, 1, 510 (1877).

† *Ibid.*, 44, 666 (1891).

‡ *Proc. Phys. Soc.*, 25, 133 (1912).

that of the electrolyte and of negligible capacity, in comparison with that of the auxiliary electrodes, p' and q' . If an electrostatic voltmeter is used, its resistance is practically infinite. Further, it is necessary that the contact potential difference between p' and q' , respectively, and the electrolyte, should not be subject to uncertain fluctuations. For this reason Smith and Moss found it best to use mercury electrodes whenever possible. Then the two contact potential differences will usually be not only constant, but also of practically identical magnitude. Any appreciable difference, if present, would affect the measurements. It can be allowed for, however, by taking the mean of the voltages obtained, when the current is passed through the electrolyte, first in one direction, and then in the opposite direction.

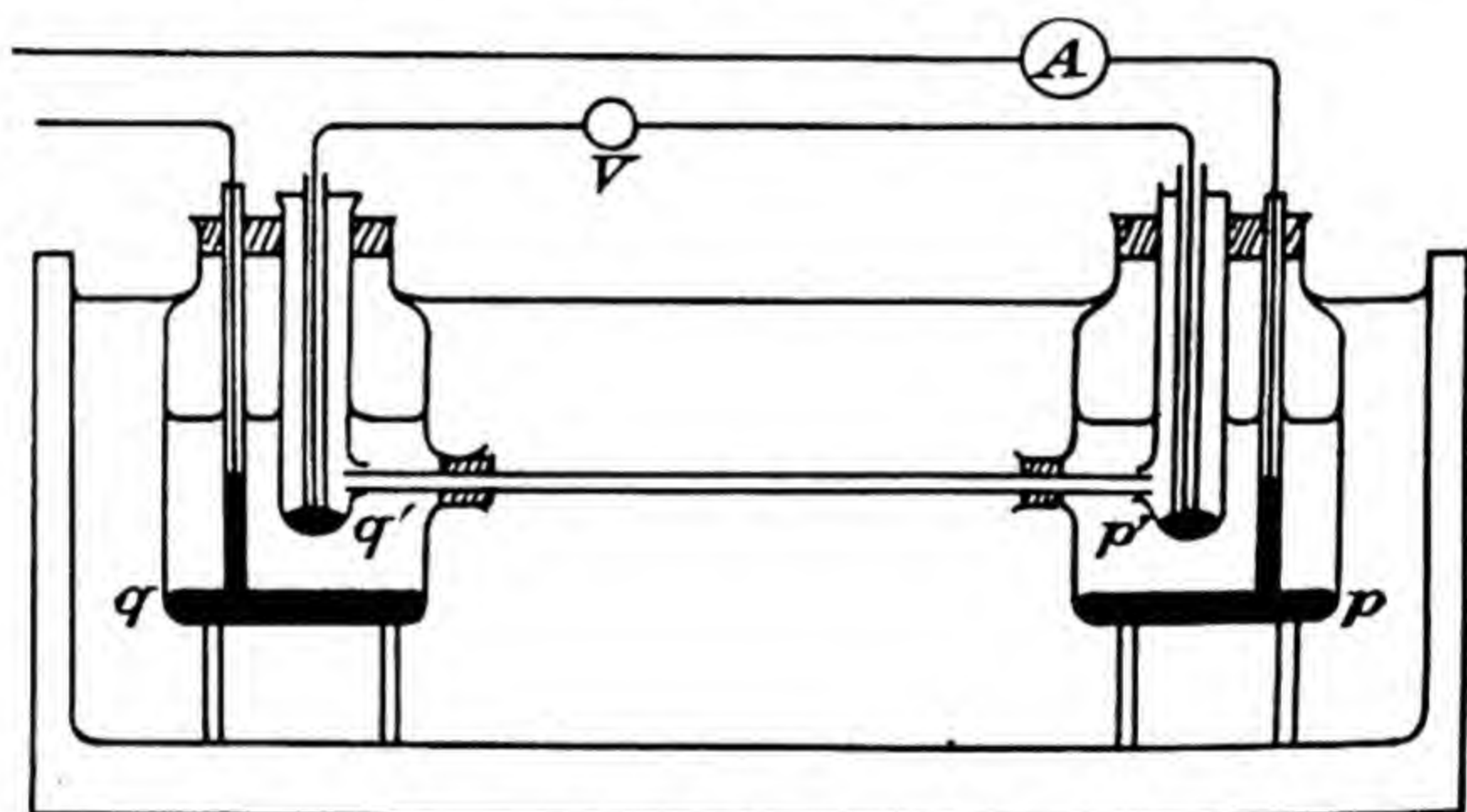


FIG. 47.—Measurement of electrolytic resistance. (Smith and Moss.)

The electrolyte was contained in a tube of 1 mm. internal diameter, 30 cm. long, connecting the two bottles in which were the main and auxiliary electrodes. The area of each main electrode was about 30 sq. cm. and that of each auxiliary electrode about 2.5 sq. cm. The apparatus was immersed in a thermostat, by means of which sudden temperature changes were avoided.

Newbery* employed the same method with the apparatus shown in Fig. 48. A small, but constant, direct current was passed between two electrodes, E_1 , E_2 , along the tube A_1 , A_2 and also through a standard resistance. Standard electrodes—calomel, mercurous sulphate, *etc.*—were constructed in the vessels C_1 , C_2 , and these were connected with a potentiometer. The extremities of the standard resistance were also connected to the same potentiometer, and by means of a commutator, the potential fall along

* *Jour. Chem. Soc.*, 113, 701 (1918).

the tube A_1 A_2 , and that across the terminals of the standard resistance were measured in rapid succession. The specific conductivity, σ , of the electrolyte was then given by

$$\sigma = \frac{l^2}{VR} \times \frac{y}{x},$$

where l is the distance between the electrode tips, A_1 A_2 , V , the volume of liquid in the tube between the same points, R , the standard resistance, and x and y , the potential differences between the electrodes C_1 , C_2 and the terminals of the standard resistance, respectively.

(b) *Methods in which the polarisation is reduced to a minimum.*—The devices for reducing the disturbing effects of polarisation are very numerous, but Kohlrausch's method, in which alter-

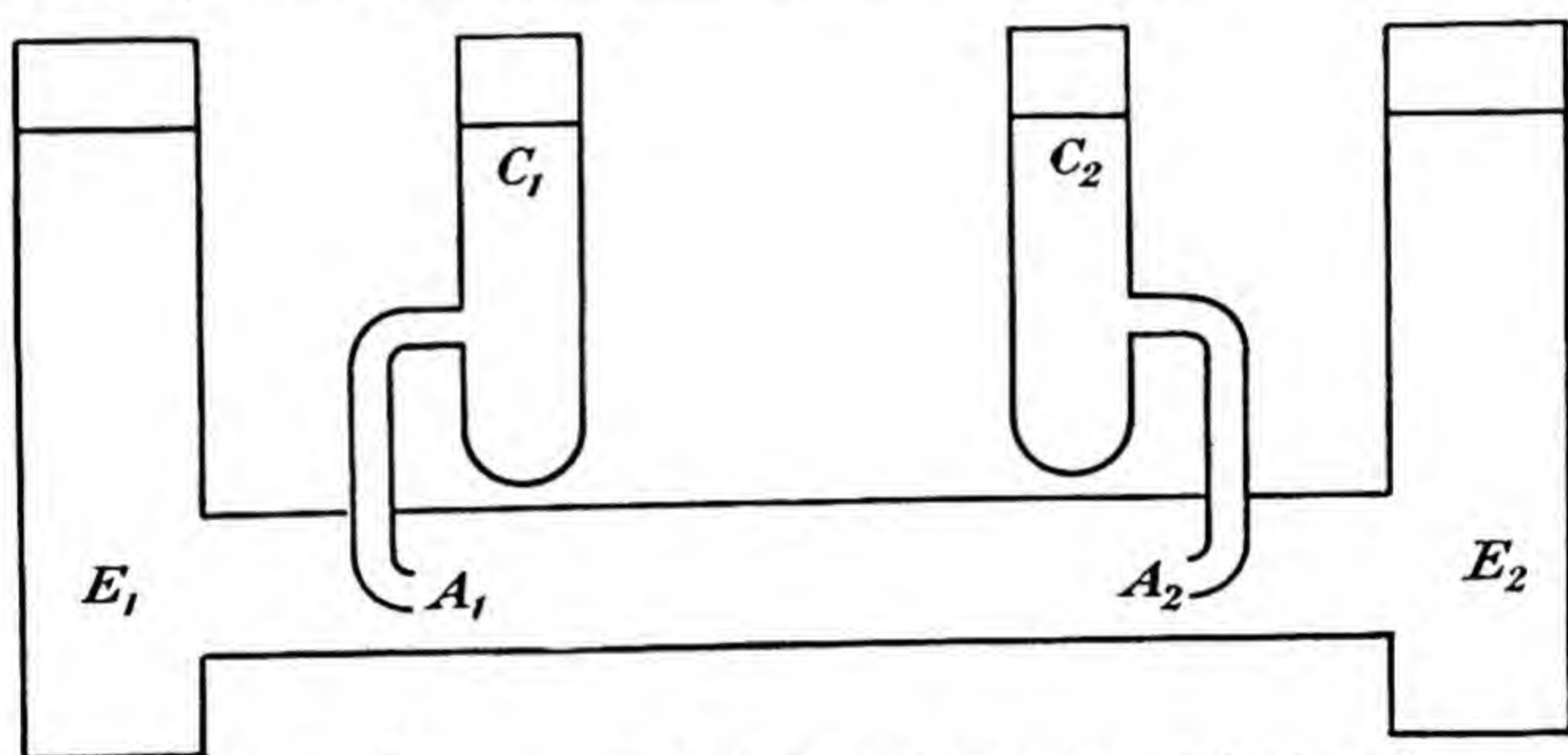


FIG. 48.—Measurement of electrolytic resistance. (Newbery.)

nating currents and a telephone are used, is superior to any method at present in use. Before describing it in detail we will consider the degree of accuracy to be expected from such an experiment. It has been shown in **section (130)** that the effective resistance of an electrolyte, placed in the arm of a Wheatstone bridge is

$$R \left(1 + \frac{P^2}{p^2 R^2} \right)^{\frac{1}{2}},$$

and that if the value of the term $\frac{P^2}{p^2 R^2}$ is negligible, the resistance measured is, approximately, the true resistance, R , of the electrolyte. The value of this term is decreased by using platinised

electrodes and a high rate of current alternation. The degree of accuracy in any particular case may be estimated as follows :—

Let R' be the effective resistance, A , the area of each electrode, and c , the capacity per unit surface area. Then $P = \frac{2}{Ac}$, and so,

$$\frac{R' - R}{R} = \frac{1}{2} \cdot \frac{4}{A^2 c^2 p^2 R^2}.$$

But $p = 2\pi n$, where n is the frequency of alternation, and if we require the value of R to an accuracy of, say 0.1 per cent., then,

$$\frac{R' - R}{R} = \frac{1}{1000} > \frac{1}{2\pi^2 A^2 c^2 n^2 R^2}.$$

For many electrodes, such as platinum, copper, and mercury, c is of the order 10 microfarads per square centimetre, hence,

$$(nAR)^2 > 5 \times 10^{11},$$

or, nAR must be greater than 7×10^5 , approximately. In the case of platinised electrodes the value of c is from 25 to 30 times

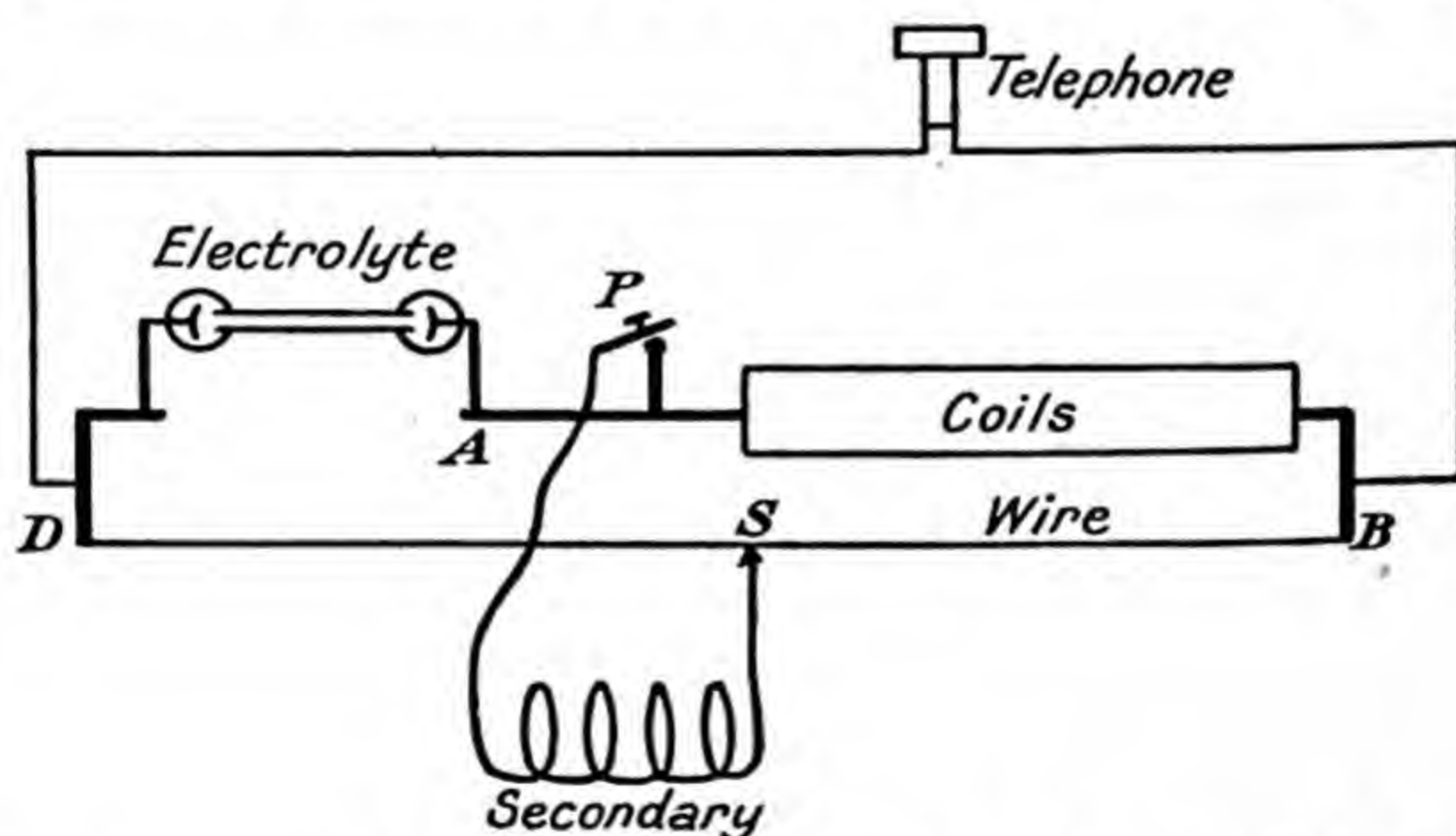


FIG. 49.—Measurement of electrolytic resistance by means of the Wheatstone bridge arrangement.

greater than that for smooth bright platinum, and so for this type of electrode nAR must be greater than 20,000.

Assuming that nAR is made sufficiently large to eliminate the polarisation effects, the electrolytic resistance is measured by means of an ordinary metre bridge arrangement, in which the battery is replaced by the secondary of an induction coil, and the galvanometer by a telephone. The make and break must be as rapid as possible, the currents not too large, and the difference in intensity

of the make and break currents should be reduced as much as possible.

Figs. 49 and 50 represent a compact and very convenient form of bridge, although greater accuracy is obtained by the use of a bridge with a longer stretched wire. The relation between the parts of this Kohlrausch bridge (Fig. 50) and those of the ordinary Wheatstone bridge will be obvious from these two diagrams. The ends of the secondary from the induction coil are brought to the points P and C, so that one end is connected to one terminal of the resistance coils, through the brass connecting plug, and to the terminal, A, by a thick copper wire, while the other end is connected to some point on the bridge wire through the sliding contact, S. The metal bar on which this contact piece slides is insulated from the right-hand pillar, E, which supports it.

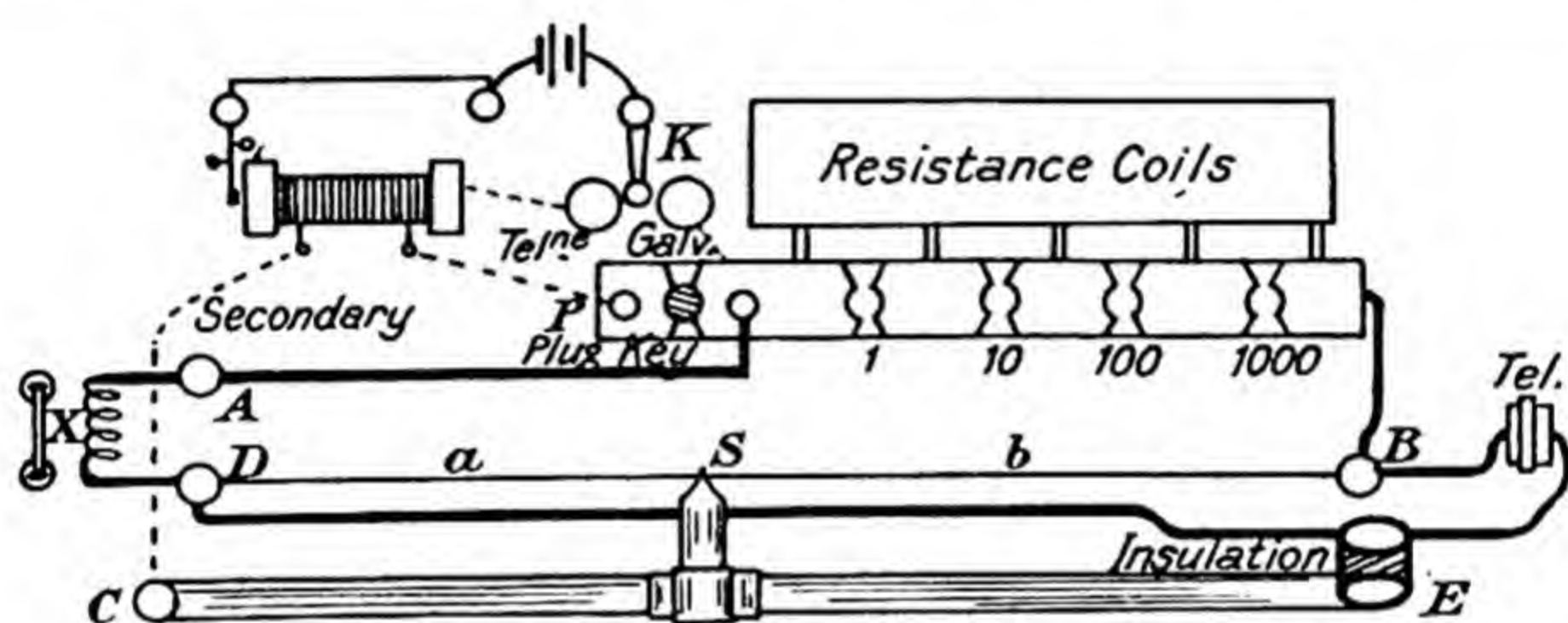


FIG. 50.—The Kohlrausch bridge.

which supports it. The screw on E, joined to D by means of a thick copper wire, serves as a convenient telephone terminal. The other telephone terminal is connected to the screw, B.

A key, K, is placed in the primary circuit, and may be connected either with the telephone, or the galvanometer, stud. The latter is connected in the circuit if direct current and a galvanometer are used. The liquid, of which the resistance is to be determined, is placed in a vessel of convenient form, and the electrodes are connected to the terminals, A and D.

A telephone must be used with alternating currents, and it should be removed to a distance from the coil, sufficient to prevent its excitation by induction. When the position of sound minimum has been determined, the following relation holds :—

$$\frac{\text{Resistance of electrolyte}}{\text{Resistance of coils used}} = \frac{a}{b'}$$

where a and b are the distances between the slider contact and the ends of the wire. Usually the bridge scale has been so divided and marked, that the ratio $\frac{a}{b}$ can be read off immediately.

132. Errors in the Kohlrausch bridge method.—The convenience, and simplicity, of Kohlrausch's method of measuring the conductivity of electrolytic solutions has been so long recognised, that at the present time no trustworthy data on this subject exist which have not been obtained by this method. There are several sources of error, however, in the method. For example, it is assumed that, by using an alternating current, all the polarisation effects are eliminated. Taylor and Acree * have shown that consistent results with simple electrolytes can only be obtained by using a perfect sine wave current, and extrapolating the results, thus found, to determine the conductivity at an infinite frequency. It seems probable that with these precautions, polarisation errors are eliminated in the case of simple electrolytes, such as potassium chloride, but when certain other electrolytes are used, especially with insufficiently polarised electrodes, it is by no means certain that decomposition of the electrolyte, with consequent polarisation of the electrodes, does not occur.

Since an electrolytic cell behaves towards an alternating current as a resistance in series with a condenser with a small leak, it forms an impedance to the harmonically varying current. Phase changes occur in that bridge arm containing the cell, and produce an unbalance in the telephone. The effect of uncompensated polarisation is always shown by the appearance of a poor minimum, silence never being obtained, and a different quality of tone is usually heard on the two sides of the minimum. It is, therefore, impossible to obtain a perfectly sharp minimum in the telephone unless the capacity effect of the cell is accurately balanced by one of several methods, such as placing (*a*) a capacity in parallel with the resistance arm of the bridge, as recommended by Kohlrausch, (*b*) a capacity in series with the resistance arm of the bridge, (*c*) an inductance in series with the cell, or (*d*) an inductance in the opposite arm of the bridge. Wien used the method indicated in (*c*) and soon discovered that the polarisation effect is not solely that of a pure condenser reactance, but that an increase in effective resistance accompanies it. In other words, the compensation of the condenser reactance, arising from the polarisation, while it improved the minimum, did not give the

* *Jour. Amer. Chem. Soc.*, 38, 2403 (1916).

correct bridge setting, but a value which corresponded to an apparent increase in the resistance of the cell.

Jones and Josephs * used a variable condenser, C_1 , in parallel with a resistance R_1 , as shown in Fig. 51, in order to compensate for the capacity of the cell, and for the source of alternating current they employed a valve oscillator, a device now commonly

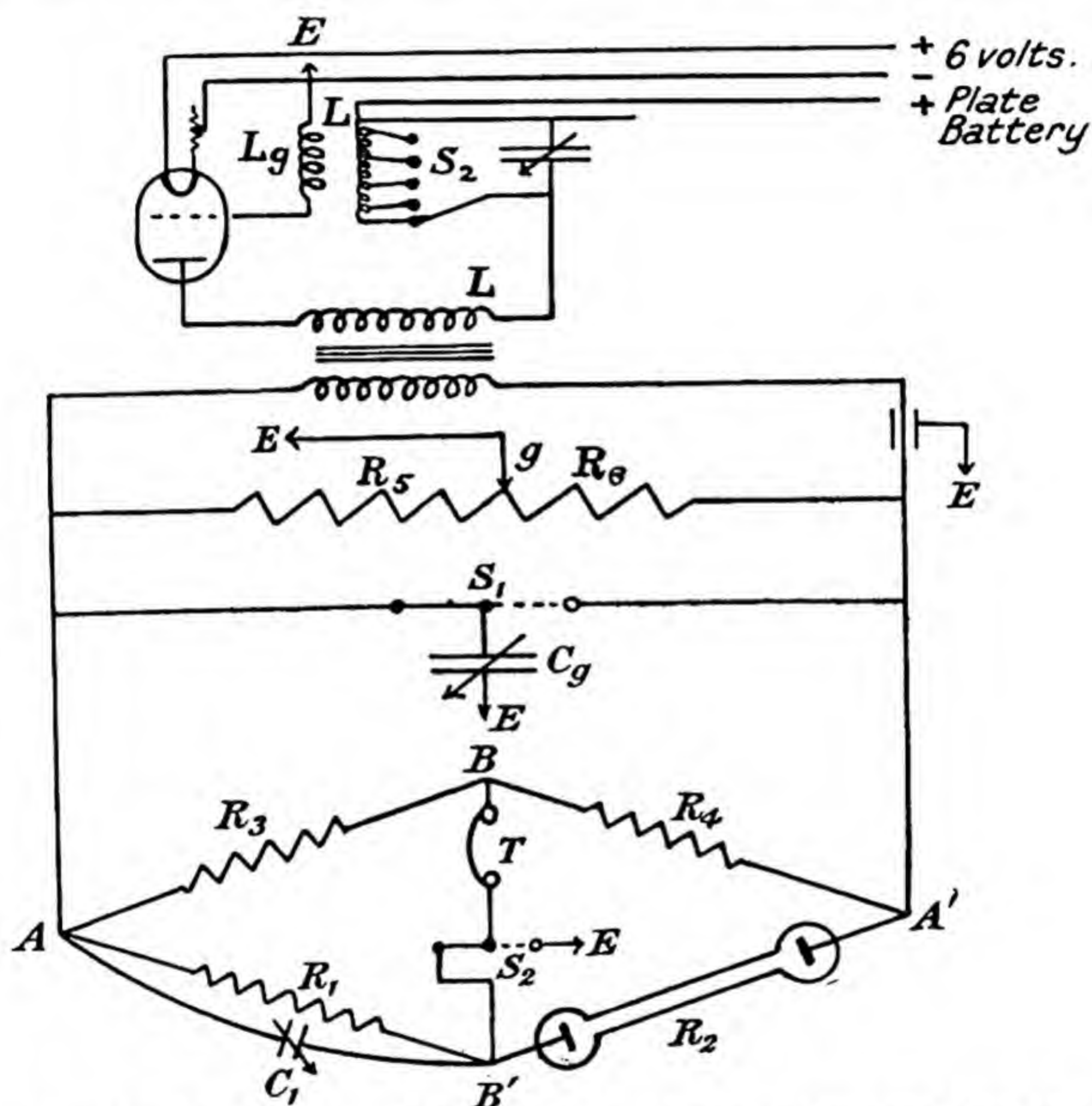


FIG. 51.—Measurement of electrolytic resistance. (Jones and Josephs.)

adopted. When the bridge is balanced, so that no current flows through the telephone, the potential of B must equal that of B' at every instant, and not only must the potentials be the same, numerically, but they must be in the same phase. The relationship

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

* *Jour. Amer. Chem. Soc.*, 50, 1049 (1928).

will only hold if the current passing along AB' is equal to that along $B'A'$, and this will not be the case if current escapes from the bridge network by ground connections, or through the capacity to the ground, *i.e.*, if there is any leakage. To overcome this difficulty the procedure adopted by these experimenters was as follows :—

- (a) They first adjusted the bridge, approximately, and then,
- (b) by means of a suitable switch, S_2 , they disconnected the telephone from B' and connected this lead wire to the earth, the other side of the telephone remaining connected to B .
- (c) The sliding contact, g , and the variable condenser, C_g , were adjusted until there was silence in the telephone. This brought the point B to earth potential.
- (d) The switch, S_2 , was then moved, so that the telephone was restored to its original position, BB' , and the connection between the telephone and the earth broken.
- (e) The bridge arm, R_1 and C_1 , was again adjusted for no sound. If this second adjustment differed much from the original, the ground adjustment was repeated, and the final bridge reading confirmed.

This arrangement and procedure ensured that B and B' were at earth potential, and, at the same time, the currents along AB' and $B'A'$ were equal, the same remark applying to the currents along AB and BA' .

Smith and Moss * had pointed out, previously, that the terminal potential difference, and the current in a branch of a network containing capacity and self-inductance, may be in the same phase although their ratio does not give the resistance of that branch. This will happen if there is leakage through the condenser, causing the potential differences between their plates to be out of *quadrature* with the current. The apparent resistance of the branch will then be a function of the frequency of the alternating current circulating in the bridge.

133. Experimental results.—Taylor and Acree † measured the conductivity of electrolytic solutions, under different physical conditions, and obtained results which are summarised below :—

(a) There is no measurable change in the resistance of a solution, or in the capacity of a cell, with a change in voltage, provided that the cells are maintained scrupulously clean and the solutions pure.

(b) There is no measurable change in the resistance of a solution with change in frequency, around 500-2,000 cycles per second,

* *Loc. cit.*

† *Jour. Amer. Chem. Soc.*, 38, 2403 (1916).

in cells with platinised electrodes. Haworth* had concluded that the resistance does vary to an easily perceptible degree with the frequency, but Smith and Moss† questioned the accuracy of Howarth's results, as they found no such variation throughout the frequency range, 100-2,300 per second.

(c) In cells with bright platinum electrodes, there is a change in resistance with a change in frequency from 600 to 1,000 cycles per second. This change varies in the following manner: (1) As the concentration of any given solution is decreased, and therefore the resistance increased, the change of resistance with frequency is decreased. (2) As the electrode surface area is increased, the change of resistance with frequency is decreased. (3) As the electrode area becomes greater, the inductance, necessary to obtain a balance, is lowered, and hence the apparent capacity is raised. (4) The higher the apparent capacity of the cell, and therefore the smaller the inductance necessary to balance this capacity, the smaller is the change of resistance with frequency. Since the apparent capacity of a cell is raised by increasing the electrode surface area, platinised electrodes should give the smallest change in the resistance with frequency and this is borne out by the experimental results. It appears that the true resistance of solutions can be measured in cells with bright platinum electrodes, only at infinite frequency.

(d) By substituting in the equation $\frac{R_n - R_\infty}{L_n n} = a$, where R_n and L_n are the resistance and inductance, respectively, at a given frequency, n , R_∞ , the resistance at infinite frequency, and a , a constant, it is possible to calculate R_∞ . The values found for R_∞ , in this manner, differ from those determined by extrapolation by $\pm 0.01 \pm 0.025$ per cent.

(e) The fact that there is a change in resistance with frequency explains why different workers have found different values for the equivalent conductance of the same solution. In some cases the measurements were made at 60 cycles per second, and in others at 1,000 cycles per second. The conductances at infinite frequency should be determined in all cases.

(f) The saturation of bright or platinised-platinum electrodes with hydrogen produces no appreciable change in the cell capacity at 60 cycles per second. This seems to indicate that the capacity does not arise simply from a neutral gas layer deposited upon the electrodes, the layer acting as an air condenser.

(g) Results show that inductance is nearly inversely propor-

* *Trans. Farad. Soc.*, 16, 365 (1921).

† *Loc. cit.*

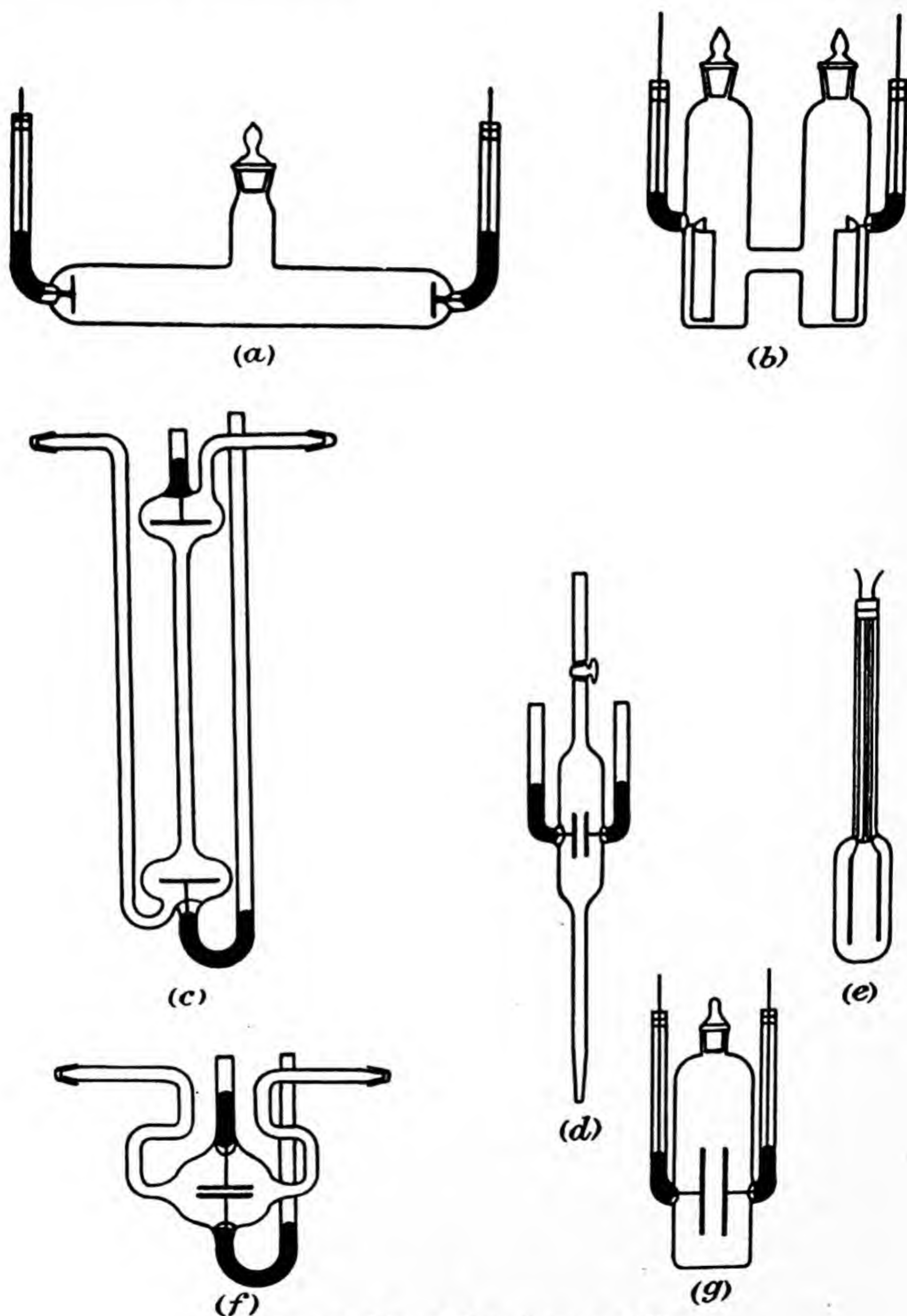


FIG. 52.—Types of conductance cells.
 (a), (b), (c), Cells for solutions of low resistance.
 (d), (e), (f), (g), Cells for solutions of high resistance.

tional to the square of the frequency. As this relation is also true for a leaky condenser, the electrolytic cell seems to act as a resistance in series with a simple leaky condenser.

134. Conductivity cells.—To obtain the specific resistance of a given electrolytic solution, from the measurement of its resistance in an electrolytic cell, of any shape or form, it is only necessary to know further the resistance of the cell when it contains a liquid of known specific resistance. Thus $R = \kappa f(k)$, where R is the resistance of the cell when it contains a liquid of specific resistance κ , and $f(k)$ is a quantity which will be independent of the nature of the liquid, if the cell is always filled to the same height, and if the electrodes always occupy the same definite positions in it. To determine $f(k)$ we observe the value of R_0 , the resistance of the cell for a liquid of known specific resistance, κ_0 , and then,

$$\kappa = \frac{R}{R_0} \kappa_0.$$

Various types of conductance cells are shown in Fig 52. They should be designed to suit the telephone which is to be used with them, and since the audibility current of the telephone is the chief controlling factor, every investigator, making conductance measurements, should determine for himself the audibility current of his telephone, since the value of this important quantity is a function, both of the construction of the telephone and of the observer's ear.

It is sometimes convenient to use a form of cell in which the conductivity and viscosity of the same sample of solution can be determined. Fig. 53 represents such a cell.* It consists of a glass tube, sealed at the bottom to a capillary arm, near the top of which is a small bulb of approximately 5 c.c. capacity. This is continued in a tube in which there is a constriction. Two marks, one just below the bulb and the second at the narrowest part of the constriction, form graduation marks of the viscometer. The top of the cell is closed by means of a glass stopper through which pass two tubes, sealed to stout

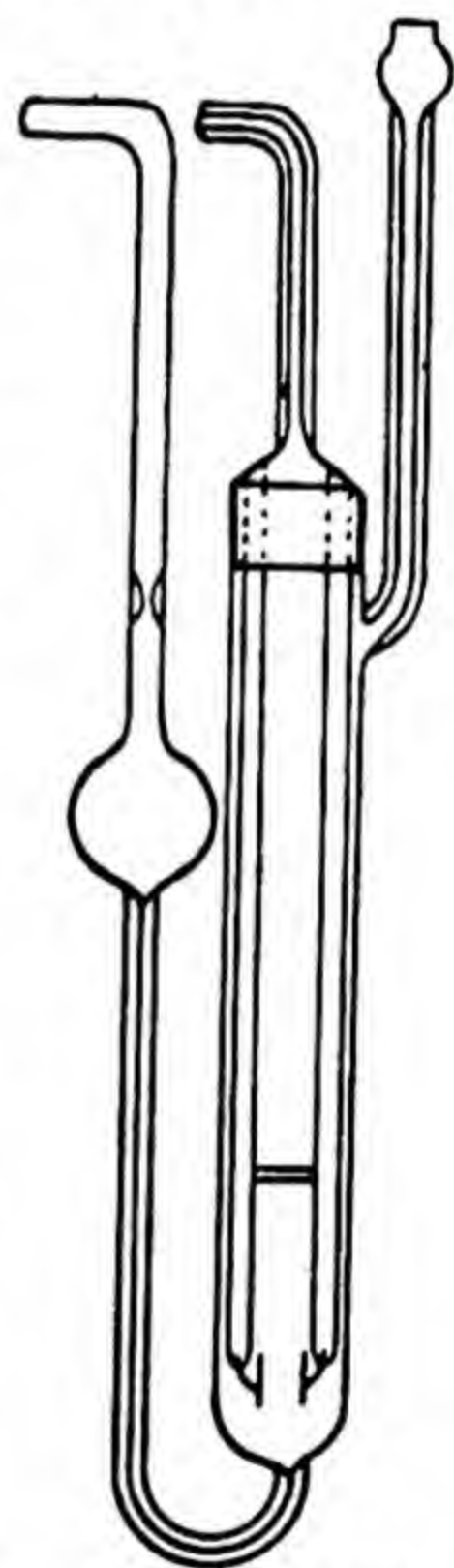


FIG. 53.—A combined conductance cell and viscometer.

* See King and Partington, *Trans. Farad. Soc.*, 23, 527 (1927).

circular platinum electrodes at the bottom of the cell. The stopper is continued in a tube of narrow bore, which is bent at right angles. Just below the stopper is a vertical side arm, ground to fit the vessel, by means of which the solutions are run into the cell.

Washburn * suggested that a cell should be designed, as regards its resistance and capacity, for the particular solution, the resistance of which is to be measured in it, and that only solutions, having resistances varying within rather narrow limits, are suitable for use with a cell of that particular resistance-capacity. Schlesinger and Read † found that the value of the cell constant depended upon the resistance of the solution by means of which it was determined. It should be known for all resistances within the range of measurements for which the cell is to be used.

Smith ‡ employed a conductance cell containing three electrodes, consisting of co-axial cylinders open at the ends, two of which were concentric and close together, the third, at some distance from the others, was arranged co-axially with respect to them. From the experimental results obtained it was shown that, as the resistance of the contained electrolyte changed, there was a variation, not only in the cell constant, but also in the ratio of the values to one another, and that the values of the equivalent conductance, determined with the aid of two cells, were concordant, only in the region of the concentration and the resistance, used to determine the cell constants. The effect of doubling the resistance of the solution between the concentric pair of electrodes was to slightly more than double the resistance of the solution between one of the concentric pair and the distant electrode. This effect amounted to about 5 per cent. at a dilution of 1,000 litres per mole, and increased with dilution, up to the highest resistance that could be measured between the distant pair of electrodes.

In measuring low electrolytic resistances, where polarisation occurs, it may be safely assumed that the cell having the greater distance between its electrodes, and exhibiting the greater resistance, will give the more reliable readings. Kohlrausch and Maltby § suggested that unplatinised electrodes may be used where the electrode area is greater than $\frac{250}{R}$ square centimetres, R , the resistance, being expressed in ohms. Parker, || however, found that the effect of polarisation was much greater than usually

* *Jour. Amer. Chem. Soc.*, **38**, 2431 (1916).

† *Ibid.*, **41**, 1727 (1919).

‡ *Ibid.*, **49**, 2167 (1927).

§ *Wiss. Abh. Phys. Tech. Reich.*, **3**, 162, 173 (1900).

|| *Jour. Amer. Chem. Soc.*, **45**, 1366 (1923).

supposed, and that an additional factor, such as the distance apart of the electrodes, must be introduced into Kohlrausch's expression. His experiments indicate that for platinised-platinum electrodes the expression, $R = \frac{160\sqrt{l}}{A}$, represents the lowest measurable resistance in ohms at which polarisation effects are negligible, where l is the distance apart, in centimetres, of the electrodes, and A , the area in square centimetres of one electrode. Probably a similar expression, $R = \frac{2500\sqrt{l}}{A}$, holds for unplatinised electrodes.

Parker discovered a new effect at high dilution with all types of cells, this effect amounting to at least 0.33 per cent. at moderate dilutions. The correction of the existing conductance data for this effect would tend to increase the values of the equivalent conductance at higher dilutions, and the limiting values would probably be affected to a considerable extent. He suggested that the effect is due to an adsorbed layer of liquid in contact with the electrodes. The correction for the resistance of this layer is assumed to be positive, or negative, according to whether the adsorbed layer contains an excess, or a deficit, of the conducting species.

As a rule, solutions of potassium chloride of known concentrations are most readily prepared, and are best adapted, for the purposes of the calibration of conductance cells. The necessary data for making up standard potassium chloride solutions, according to the weight method, for calibrating cells, are correctly given by Kohlrausch and Holborn* for 1.0 normal solutions only, and their directions for making up standard solutions of concentrations, 0.1, 0.02, and 0.01 normal are incorrect. For the 0.1 normal solution the error is 0.10 per cent., and for the 0.01 normal solution, 0.54 per cent.

Kraus and Parker† determined the specific conductance of a 0.1 normal solution of potassium chloride at 25° C. in terms of its value at 18° C. Assuming the value 0.011203 for the specific conductance at 18° C., as determined by Kohlrausch and Maltby, Kraus and Parker obtained the value 0.0128988 for the specific conductance at 25° C. In general, conductivity measurements are now made at 25° C.

135. Conductivity water.—It is evident that reliable data for the conductivity of dilute solutions can only be obtained by

* *Das Leitvermögen der Elektrolyte* (1916).

† *Jour. Amer. Chem. Soc.*, **44**, 2422 (1922).

the use of highly purified water under such conditions that no contamination takes place during the measurements, or, by determining the nature and the amount of the impurities present in the water, and then applying corrections from the mass action relation.

For special pure water Kohlrausch and Heydweiller * give the following values :—

Original specific conductivity of water in vacuo :

$$0.05 \times 10^{-6} - 0.11 \times 10^{-6} \text{ ohm}^{-1}.$$

Specific conductivity after 20 minutes' exposure to air :

$$0.34 \times 10^{-6} - 0.40 \times 10^{-6} \text{ ohm}^{-1}.$$

Specific conductivity after long exposure to air :

$$0.66 \times 10^{-6} - 0.65 \times 10^{-6} \text{ ohm}^{-1}.$$

The final values obtained for different samples, in equilibrium with the atmosphere, were practically of constant value, $0.65 \times 10^{-6} \text{ ohm}^{-1}$ at 18°C . Subsequent investigators have recorded uniformly similar results, and it is impossible to maintain, for more than a short time interval, any sample of water, in contact with air, at a much lower value. The endeavours of later workers have been almost entirely directed towards facile preparation of large quantities of water, of as low a specific conductivity as possible when in contact with air.

Walker and Cormack † prepared water of specific conductivity $0.75 \times 10^{-6} \text{ ohm}^{-1}$, at 18°C ., by three successive distillations, with alkali, with phosphoric acid and without the addition of any chemical to the water. Kendall ‡ found that one distillation from tap water, to which a few cubic centimetres of Nessler's solution had been added, provided water of $0.9 \times 10^{-6} \text{ ohm}^{-1}$ specific conductivity, at 25°C . Distillation was carried out in the open air in Jena glass vessels.

In order to bring the accuracy of conductance data for dilute solutions to within $\frac{1}{100}$ of 1 per cent. it is necessary to use ultra-pure conductivity water, to carry out all experimental operations in an atmosphere free from conducting impurities, and to employ quartz cells. The conductivity of ultra-pure conductivity water is $0.043 \times 10^{-6} \text{ ohm}^{-1}$, and this value was reached by Bencowitz and Hotchkiss § after forty-two back and forth distillations in vacuo, at a low temperature. The glass conductivity cell, in which

* *Ann. d. Phys.*, 53, 209 (1894).

† *Jour. Chem. Soc.*, 77, 5 (1900).

‡ *Jour. Amer. Chem. Soc.*, 39, 7 (1917).

§ *Jour. Phys. Chem.*, 29, 705 (1925).

the measurement was made, had been standing for ten years, and only a small quantity of water was prepared.

Pure distilled water is a saturated solution of carbonic acid, and its specific conductivity, $0.6 \times 10^{-6} \text{ ohm}^{-1}$, is the same as that of a saturated solution of carbonic acid, under atmospheric conditions. A permanent lower value for water in contact with air is not possible, since slow absorption of carbon dioxide must take place, unless airtight vessels are used, until equilibrium is attained.

136. Correction for the conductivity of water.—As a rule, the specific conductivity of water, used in conductance experiments, is $0.7 \times 10^{-6} \text{ ohm}^{-1}$, and the use of such water involves a correction for the conductivity of the solvent which may amount to 8 per cent. for a 0.0001 normal solution, and to 44 per cent. for a 0.00001 normal solution. Usually the value of the specific conductivity of the water is subtracted from the total conductivity of the solution. This is the normal solvent correction, and is based on the assumption that the various ions present have no influence upon each other's conducting power, but this assumption fails to take into account several factors which depend upon the interionic forces. A true solvent correction must recognise the effect which the presence of the solute ions exerts upon the mobilities of the solvent ions, and *vice versa*. In addition, the use of glass cells influences the results to a somewhat greater extent than the impurities present in the water.

When carbon dioxide dissolves in water, we assume that the acid H_2CO_3 is formed. The conductivity and equilibrium constant of such solutions have been measured by Pfeiffer,* Knox,† Walker and Cormack,‡ and Kendall,§ and from the conductivity measurements, it is possible to calculate the value of the specific conductivity of pure water, saturated with carbon dioxide, at a pressure equal to the partial pressure of the gas in the atmosphere. Thus, at 18°C . and 760 mm. pressure, the solubility of this gas is 0.0414 moles per litre. Taking the partial pressure of carbon dioxide in air as 3×10^{-4} atmosphere, the number of moles per litre in a solution, saturated at this pressure, will be $0.0414 \times 3 \times 10^{-4} = 1.25 \times 10^{-5}$. If, then, in the dilution formula,

$$\frac{\alpha^2 C}{(1 - \alpha)} = K,$$

* *Ann. Phys. Chem.*, **23**, 625 (1884).

† *Ibid.*, **54**, 44 (1895).

‡ *Jour. Chem. Soc.*, **77**, 5 (1900).

§ *Jour. Amer. Chem. Soc.*, **39**, 7 (1917).

we substitute 3.04×10^{-7} for K , and 1.25×10^{-5} for C , we obtain $\alpha = 0.144$, so that 14.4 per cent. of the carbonic acid, dissolved from normal air by pure water, is dissociated into H^+ and HCO_3^- ions. Taking the molecular conductivity of the solution at infinite dilution to be 336 ohm^{-1} , at 18° C. , we obtain a value $336 \times 0.144 = 48.4$ for the molecular conductivity of the saturated solution. From this, the specific conductivity is obtained on multiplying by the number of moles per cubic centimetre, so that we have the value $48.4 \times 1.25 \times 10^{-8} = 0.605 \times 10^{-6} \text{ ohm}^{-1}$ for the specific conductivity of water, which has been in contact with the atmosphere, at 18° C. This result is in excellent agreement with the experimental values, and therefore we infer that carbon dioxide is the only substance in the atmosphere which confers conductivity upon the water.

If carbonic acid is the impurity present in a solution of a weak acid, each acid will lower the dissociation, and therefore the conductivity, of the other, and the correction for the impurity will not be as large as it appears to be at first sight. Suppose that the conductivity of a weak acid has been measured at 18° C. , and that C , $[C_1]$ and $[C_2]$ are the concentrations of the acid, the anions of the acid, and the HCO_3^- ions, respectively. The equilibrium constant, K , of the weak acid, which may be determined experimentally, is given by **section (59)**,

$$\frac{\{[C_1] + [C_2]\}[C_1]}{C - [C_1]} = K_1.$$

For carbonic acid, at 18° C. , formed from a saturated solution of carbon dioxide, under the partial pressure at which the gas exists in the atmosphere,

$$\frac{\{[C_1] + [C_2]\}[C_2]}{1.25 \times 10^{-5} - [C_2]} = K_2 = 3.04 \times 10^{-7},$$

where 1.25×10^{-5} is the concentration, in moles per litre, of a solution (saturated) of carbonic acid. Hence both $[C_1]$ and $[C_2]$ may be calculated, and we can obtain the concentration of the HCO_3^- ions, and the number of H^+ ions arising from the carbonic acid in the water. From this we can determine the concentration of the H^+ ions derived from the weak acid. The conductivity of the carbonic acid can be determined from the calculated value of $[C_2]$, but we are not justified in assuming that the corrected conductivity of the solution is equal to the difference between the observed conductivity of the electrolytic solution and that of the carbonic acid, since this difference would give the conductivity of the acid in the presence of carbonic acid. The

product of the concentrations of the H^+ ions and the anions, present in the solution containing carbonic acid, must be equal, approximately, to the product of similar quantities in an ideal aqueous solution of the weak acid, *i.e.*, one containing no carbonic acid, since the water concentration in the two solutions remains, approximately, the same. Let $[C_3]$ be the concentration of the anions of the weak acid under these ideal conditions, so that we may write

$$\frac{[C_3]^2}{C - [C_3]} = \frac{\{[C_1] + [C_2]\}[C_1]}{C - [C_1]}$$

or, since the values of $[C_1]$ and $[C_3]$ are very small compared with that of C ,

$$[C_3]^2 = \{[C_1] + [C_2]\}[C_1],$$

and since

$$\{[C_1] + [C_2]\}[C_1] = \{C - [C_1]\}K_1 = [C_3]^2,$$

$$[C_3] = \sqrt{CK_1}, \text{ approximately.}$$

If σ is the corrected specific conductivity, and Λ_{cor} the corrected equivalent conductivity,

$$\sigma = \frac{C\Lambda_{\text{cor}}}{10^3},$$

and since

$$\alpha = \frac{\Lambda_{\text{cor}}}{\Lambda_0} = \frac{[C_3]}{C},$$

where Λ_0 is the equivalent conductivity at infinite dilution,

$$\sigma = \frac{[C_3]\Lambda_0}{10^3}.$$

137. Conductivity of very weak solutions.—In measuring the conductance of dilute solutions it is necessary, on the one hand, that all the electrolyte present shall be in a known state, and, on the other hand, that the specific conductance, due to this electrolyte, shall be determinable. Except in a few cases, impurities in the water have little influence upon the state of the *salt* in solution. At the same time, any impurities present are not necessarily influenced by the presence of the *salt*, and, accordingly, the conductance due to these impurities may be corrected for, by measuring the conductance of the water from which the solutions were made. With solutions of *acids* and *bases* this is not the case. If the impurity, present in the water from which an acid solution is made, contains a base, or the salt of a weak acid, then the concentration of the acid will be influenced by the presence of the impurity. Furthermore, the correction to be

applied cannot be determined by measuring the conductance of the original solvent. For example, it was found in the early days, that the equivalent conductivity of an acid, instead of approaching a limiting value asymptotically, as the dilution increased, passed through a maximum, after which it decreased as the concentration was lowered. It has been suggested that this effect is brought about by the presence of a base, or a salt of a weak acid, in the solvent, as a result of which a certain amount of the hydrogen ion disappears on reaction with the base, the equivalent conductance being decreased accordingly.

The influence of impurities in water, including alkalis from

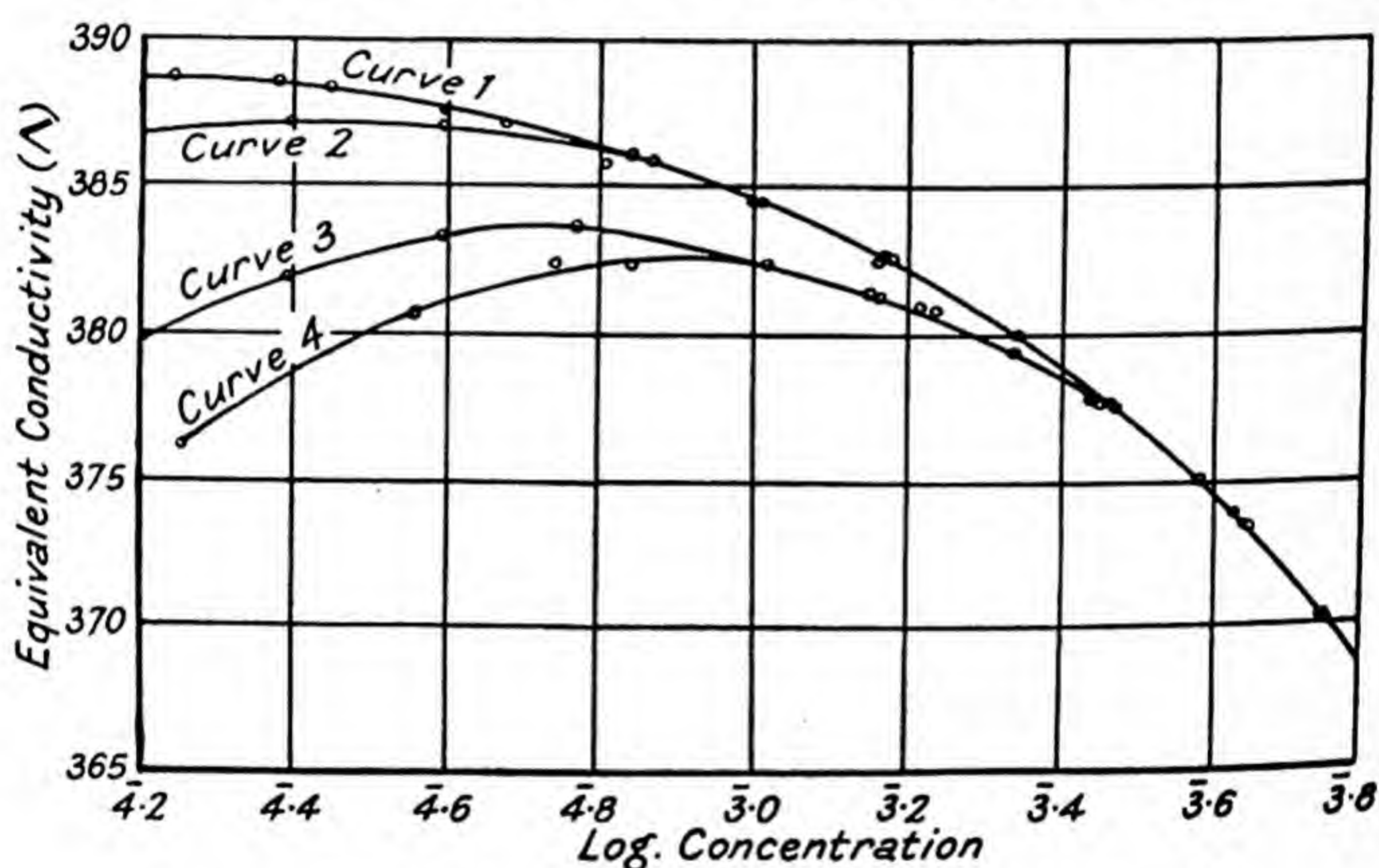


FIG. 54.—Effect of impurities on the conductance of iodic acid.

the glass cells, is illustrated by the results of Kraus and Parker* for iodic acid, shown in Fig. 54, in which values of the equivalent conductance have been plotted against the logarithms of the concentrations, as abscissæ. Curve 1 was obtained using quartz cells, and water of specific conductivity $0.095 - 0.38 \times 10^{-6} \text{ ohm}^{-1}$; curve 2, with another quartz cell, and water of $0.5 \times 10^{-6} \text{ ohm}^{-1}$; curve 3, with soda glass and water of $0.24 \times 10^{-6} \text{ ohm}^{-1}$; and curve 4, with the same cell but with water of $0.8 \times 10^{-6} \text{ ohm}^{-1}$, specific conductivity. It is seen that, with quartz cells and the purest water obtainable, a maximum does not occur in the conductance curve, down to the lowest

* *Jour. Amer. Chem. Soc.*, 44, 2429 (1922).

concentrations used. Curve 2 shows a slight maximum, and, therefore, the difference between curves 1 and 2 must arise from the influence of impurities in the water. The pronounced maximum in curve 3 is attributed to the influence of alkalis from the glass, and the difference between curves 3 and 4 to other impurities in the water.

The weaker acids showed no maximum down to concentrations 0.0002 normal; in fact, the maximum point cannot appear until the decrease in the conductivity, due to the presence of impurities, overbalances the increase arising from the increased ionisation with dilution. The weaker the acid, the greater is the relative conductivity change for a given change in the concentration. Consequently, it is only in the case of the strong acids that the effect is observed at higher concentrations.

Kraus and Parker also noticed that, when acid solutions of concentration about 0.002 normal were introduced into glass cells, the resistance increased by 0.04 per cent., after the lapse of 30 minutes. This effect appears to be due to the fact that the concentration of the impurities, coming from the glass walls, is greater near the walls than at the electrodes.

Whetham* found that, within the limits of experimental error, the equivalent conductance of a dilute acid is unaffected by boiling under reduced pressure, although the conductance of the solvent is thereby much reduced. The equivalent conductance of an acid is also unaffected by the addition of a small quantity of potassium chloride to the water. A little carbon dioxide gas, added to a sulphuric acid solution, however, considerably reduces the equivalent conductance of the solution.

Whetham seeks to explain the apparent diminution in the equivalent conductance of acids and alkalis at extreme dilutions by the association of ions, brought together in solution. Such an association would take place if the solvent contained (a) a weak acid, such as carbonic acid; (b) a weak alkali, such as ammonia; (c) a salt, formed by the neutralisation of the weak acid by the weak alkali, for example, ammonium carbonate. For a given conductivity, ammonium carbonate is more effective in reducing the conductivity of a solution of sulphuric acid than ammonium, or carbonic acid, present separately.

138. Polarisation capacity.—From what has been said in **section (130)** an electrolytic cell, consisting of platinum electrodes in sulphuric acid, possesses polarisation capacity, when an electric current is sent through it, and this capacity, c , can be

* *Proc. Roy. Soc., A*, 76, 577 (1905).

counterbalanced by a self-inductance, L , if $c = \frac{1}{Lp^2}$, where $p = 2\pi n$, n being the frequency of the alternating current. Thus, the value of c may be determined experimentally, if L is known, when such a balance is obtained. One method of measuring this polarisation capacity was used by Haworth,* the arrangement of his apparatus being shown in Fig. 55. The electrolytic cell is denoted by the resistance R in series with a condenser, C . In series with it is placed a variable self-inductance, L_1 , and in the adjacent arm of the bridge, another self-inductance, L_2 , is introduced to balance the minimum self-inductance of the variable one, when the electrolytic cell is short-circuited. The bridge is balanced, initially, with the cell short-circuited. The latter

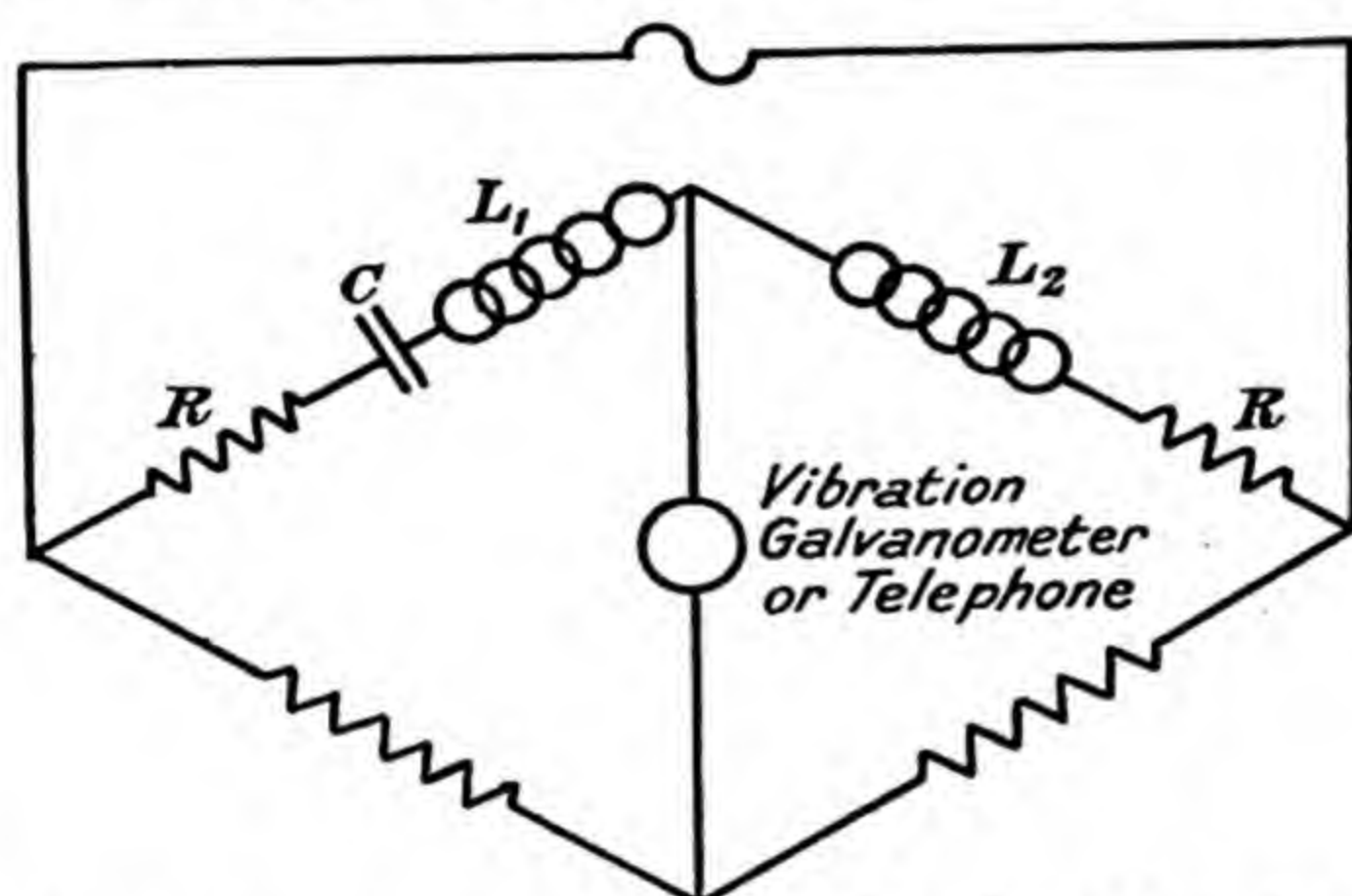


FIG. 55.—Measurement of the capacity of an electrolytic cell.

is then introduced, and balance again obtained by introducing self-inductance in the cell arm and resistance in the adjacent arm. The cell capacity is then given by the formula

$$c = \frac{1}{(L_1 - L'_1)p^2},$$

$L_1 - L'_1$ being the difference between the initial and final values of the self-inductance, L_1 . The alterations in the resistance and self-inductance must proceed simultaneously, and the above relation only holds, provided that the capacity is a constant quantity during the current cycle. If it varies, the current wave will be distorted, and absolute balance will be impossible.

Hey † describes another method of measuring the polarisation capacity. Across the electrolytic cell is placed a condenser of

* *Trans. Farad. Soc.*, 16, 365 (1921).

† *Jour. Sci. Inst.*, 4, 401 (1927).

known capacity, and the system is short-circuited. The short-circuit is broken, and a second condenser of known capacity is charged to a known potential, and then discharged into the system. The first condenser is disconnected from the electrolytic cell, and from the second condenser, and then discharged through a ballistic galvanometer. Thus, the potential difference attained by the cell, which is the same as that of the first condenser, can be calculated. It is impracticable to determine the potential difference from a discharge of the second condenser because of the residual effects. Since the depolarisation of the cell is rapid, the potential difference immediately after the discharge of the second condenser into the system is deduced by varying continuously the time of contact of the cell with the first condenser.

In determining the capacity at different frequencies, Merritt * developed an alternating current, of the desired frequency, by means of an oscillating valve, and a loosely coupled secondary circuit, tuned to resonance by means of its adjustable condensers. When the cell was placed in series with the variable condenser, it was necessary to make a small change in the setting in order to restore resonance. This change in capacity of the variable condenser is equal to the electrolytic capacity.

The capacities of electrolytic cells, acting as leaky condensers, vary with the solution, size of electrode, character of surface, resistance and other factors. The values range from 10 to 1,000 microfarads per sq. cm. for bright electrodes, and from 500 to 5,000 microfarads per sq. cm. for platinised electrodes.† Warburg ‡ predicted that the polarisation capacity would vary inversely as the square root of the current frequency. Merritt's results are, in the main, in agreement with this theory, but within the range $n = 4,000,000 - 500,000$ the capacity appears to be inversely proportional to the frequency. There is some reason to expect such a change in the law at high frequencies, since Warburg's theory is based upon the assumption that the ions are so numerous, that equilibrium between the ionic concentration in the liquid and that in the electrode can be established instantly, and without appreciable change in the concentration within the liquid. At sufficiently high frequencies this assumption must be modified.

Wolff § has found that the law relating capacity with frequency changes between 3,000 and 100,000 cycles per second. He attributed this change to a true polarisation capacity effect, but the

* *Phys. Rev.*, **17**, 524 (1921).

† See Taylor and Acree, *Jour. Amer. Chem. Soc.*, **38**, 2403 (1916).

‡ *Ann. d. Phys.*, **4**, 303, 492 (1899); **6**, 125 (1901).

§ *Phys. Rev.*, **27**, 755 (1926).

capacity depended very much upon the particular pieces of metal used as electrodes in the cell, and even for the same piece it varied considerably under different conditions.

The measurements of Pierce * suggest that $cp^{0.15}$ is constant over the frequency range 512-1,024 cycles per second. This relationship cannot hold at $p = 0$, since in this case c would be infinity, whereas the capacity has a finite value at zero frequency, *i.e.*, with direct current.

Using platinised and unplatinised - platinum electrodes in potassium chloride, Haworth † measured the capacity of the resulting cells at various frequencies. His results, at 18° C., are given in Table LXIV.

TABLE LXIV.

CAPACITY OF ELECTROLYTIC CELLS AT DIFFERENT FREQUENCIES.

Strength of KCl Solution.	Cell with Platinised Electrodes.		Cell with Unplatinised Electrodes.	
	Capacity at Frequency 1,000 cycles per sec. (m. farads).	Capacity at Frequency 100 Cycles per sec. (m. farads).	Capacity at Frequency 1,000 Cycles per sec. (m. farads).	Capacity at Frequency 100 Cycles per sec. (m. farads).
0.1N	4,200	27,000	81	120
0.05N	3,620	16,550	85	121
0.025N	2,260	10,600	69.6	106
0.0125N	1,622	6,810	68.5	98
0.00625N	1,072	4,540	59.0	103
0.003125N	1,072	3,040	54.7	77
0.0015625N	633	1,760	59.8	79
0.00078125N	108	1,282	36.1	68

These results show that the effect of platinising the electrode is not simply to increase its area. If this were so, the ratio of the capacity effect at the platinised electrodes, to that at the unplatinised electrodes would remain constant, for different frequencies and strengths of the solutions, but this is not the case. The effect of platinising appears to produce a deposit of spongy platinum, which is capable of more or less absorbing the gas film, arising from polarisation. Thus, the enormous increase of capacity, observed with the platinised electrodes, is not due to the increased area of the electrodes, but to the diminished thickness of the gas film.

The polarisation capacity decreases as the current passing through the electrolytic cell is decreased, but approaches a so-

* *Phys. Rev.*, 31, 470 (1928).† *Loc. cit.*

called initial capacity. Miller * showed that the latter varied nearly directly as the one-fourth power of the concentration of the electrolyte.

139. Resistance of fused electrolytes.—As a rule, the ordinary Wheatstone bridge arrangement with coil and telephone is not suitable for use with fused electrolytes, since their resistances are too small to be accurately measured. Fleck and Wallace † found that this was so with fused sodium hydrate. They employed an iron vessel in the form of an inverted cone, 4 feet deep and 4 feet in diameter, which held nearly a ton of molten caustic soda, and measured the currents and the corresponding voltage drops between the electrodes. When these values were plotted, they lay on a straight line. The actual resistance, at 360°C. , was about 0.2 ohm, and decreased with temperature, thus following the well-known law of resistance variation of aqueous solutions with temperature.

These experimenters showed that, if a constant current was passed between two electrodes, placed close together and immersed in the fused caustic soda, and the two electrodes were moved apart, the resistance increased until a certain maximum value was reached, after which it remained constant. When the current was passed through the fused electrolyte between sodium electrodes, Ohm's law was followed, and thus, in the fused electrolyte, the ions are already in existence. No energy is required to disrupt the sodium hydrate molecule.

Biltz and Klemm ‡ measured the conductivity of fused metal chlorides, using a sinusoidal alternating current of 500 periods per second at 4 volts with a bridge and telephone arrangement. A quartz U tube, fitted with platinised-platinum electrodes, was employed as the containing vessel, and access of water was excluded. The constant of the cell was determined by calibrating with a potassium chloride solution. They investigated the effect of varying the capacity of the cell and form of the electrodes on the conductance values of fused salts. With disc-like electrodes the specific conductivity increased with capacity, but reached a limiting value which agreed with that given by other forms of electrodes.

In the case of the alkali chlorides the specific conductivity values for the fused salt were, at temperatures near the melting-point, $\text{LiCl} - 5.94$, $\text{NaCl} - 3.56$, $\text{KCl} - 2.19$, $\text{RbCl} - 1.55$, $\text{CsCl} - 1.14\text{ ohm}^{-1}$. The molecular conductivity, k , is defined as the

* *Phys. Rev.*, 22, 622 (1923).

† *Trans. Farad. Soc.*, 16, 346 (1920).

‡ *Zeits. phys. Chem.*, 110, 318 (1924).

product of the specific conductance and molecular volume, as derived from the density. These experimenters found that the values of the molecular conductivity, at the melting-point, varied with the molecular volume, v . For the alkali chlorides $kv^{\frac{2}{3}}$ was approximately constant and equal in value to that for the chlorides of the alkaline earths, while in the case of the chlorides of silver, cadmium and bismuth the value of the function was much lower.

BIBLIOGRAPHY.

- Banerji, Trans. Farad. Soc., 22, 111 (1926).
Becker, Zeits. Elektroc., 32, 305 (1926).
Bencowitz and Hotchkiss, Jour. Phys. Chem., 29, 705 (1925).
Chapman and Hibbard, Tech. Bull., No. 23.
Davies, Trans. Farad. Soc., 25, 129 (1929).
Elsas, Wied. Ann., 42, 165 (1891).
Fürth, Zeits. Elektroc., 32, 467 (1926).
Goodwin and Haskell, Amer. Acad. Proc., 40, 399 (1904).
Grindley and Davies, Trans. Farad. Soc., 25, 133 (1929).
Hartley and Barrett, Jour. Chem. Soc., 103, 786 (1913).
Hollard, Jour. de Phys. et le Rad., 7, 25 (1926).
Knox, Ann. Phys. Chem., 54, 44 (1895).
Kohlrausch and Holborn, Leitvermögen der Elektrolyten.
Marie and Noyes, Jour. Amer. Chem. Soc., 43, 1095 (1921).
Merritt, Phys. Rev., 17, 524 (1921).
Pfeiffer, Ann. Phys. Chem., 23, 625 (1884).
Redman, Jour. Phys. Chem., 29, 1548 (1925).
Smith, Jour. Amer. Chem. Soc., 49, 2167 (1927).
Stroud and Henderson, Proc. Phys. Soc., 15, 13 (1896).
Walker and Cormack, Jour. Chem. Soc., 77, 5 (1900).
Washburn, Jour. Amer. Chem. Soc., 40, 122 (1918).
Wien, Ann. d. Phys., 59, 267 (1896).

CHAPTER X.

THEORIES OF ELECTROLYTIC SOLUTION.

140. Preliminary considerations.—There are two aspects to the problem of electrolytic conduction, namely, the well-defined equilibria which exist in solutions, and the mechanism whereby the conduction process is effected. As regards the equilibria, we apply the principles governing them, and support them by various assumptions, which involve an equation of state of the system. The precise form of this equation is not known, and thus no general solution of the problem can be reached by this method. On the other hand, a theory of the conduction process demands a precise knowledge of the forces that occur between the charged particles and their surroundings. If we assume a force function, statistical methods can be employed to find a solution, and these statistical methods are now being developed and applied to electrolytic systems. As would be expected, the simplest type of problem is that in which the electrolytic concentration is so small that the interaction between the ions and the other species present, even if not negligible, becomes calculable. At low concentrations, however, the experimental data are uncertain and it is difficult to compare results, deduced from theory, with those obtained experimentally. Lately, however, great success has attended the efforts of Debye and Hückel who have developed, from purely theoretical considerations, the law connecting equivalent conductivity with concentration, which Kohlrausch had found empirically many years ago, namely,

$$\Lambda = \Lambda_0 - \sqrt{C}.$$

The ionic theory of electrolytic solutions has met with marked success, not only in explaining conductance problems, but also in the allied problems, such as those involving osmotic phenomena, including freezing-point temperature depression, and boiling-point temperature elevation.

Many theories have been proposed to represent the actual nature of electrolytic solutions, some of which do account for the

properties of one type of electrolyte, such as a weak one, but fail when applied to strong electrolytes. Some of these theories will now be considered.

141. Ostwald's dilution law.—We have already mentioned in Chapter III. some of the various formulæ which have been put forward to represent the relation between the equivalent conductance and the concentration of electrolytic solutions. One of the first, and certainly the most important one originally, was Ostwald's dilution law, which has been developed in **section (14)** by means of an extension of the mass action law. The latter has been theoretically and experimentally verified for dissociation of gases, and it was extended to the equilibrium, which is assumed to exist, between the molecules of a salt in dilute solution and the ions of the salt. It is supposed that on entering into solution the salt molecules disappear, to a greater or less degree, their place being taken by electrically charged particles—ions. Under these conditions, when equilibrium is established, we obtain Ostwald's familiar dilution law, namely,

$$\frac{C\alpha^2}{1 - \alpha} = K.$$

Experimental investigation on the conductances of dilute solutions led to the result that the equation is satisfactorily applicable to the cases of weak organic acids, but strong acids and bases, and their salts, give results which are widely divergent from the theory. Weiland* has shown from the conductivity data for solutions of potassium chloride, over the concentration range 0.00001-0.001 normal, that K has a constant value in the case of solutions for which C is less than 0.0001N. This result is regarded as direct evidence in favour of the validity of the mass action law in its application to the ionisation of potassium chloride at very low concentrations. Arrhenius† had previously expressed the view that the measurements of Kohlrausch and Maltby,‡ on sodium chloride solutions, were such as to indicate that the ionisation is governed by the mass law at high dilutions, and the supposition that the law is generally applicable, under such conditions, is shared by Washburn,§ who contends that the equilibrium constant, K , has the same value for all univalent salts of strong acids and bases. Other investigators|| also conclude that the

* *Jour. Amer. Chem. Soc.*, **40**, 131 (1918).

† *Medd. K. Vetenskapsakad.*, Nobel Inst., **2**, No. 42 (1913).

‡ *Sitz. Akad. Wiss. Berlin*, **36**, 665 (1899).

§ *Jour. Amer. Chem. Soc.*, **40**, 150 (1918).

|| *Trans. Farad. Soc.*, **15**, 3 (1919).

values of K for different salts of the type MX remain identical at concentrations that are appreciably greater than those for which the mass action law holds, and this identity persists up to concentrations that increase, as the salts under comparison resemble each other more and more closely.

Apart from the evidence which has been brought forward in favour of the operation of the mass law at higher dilutions, it must be recognised that the law fails completely to account for the general behaviour of the strong electrolytes, more particularly in the region 0.0001-0.01 normal. These divergencies may be explained thus :—*

(a) The errors incident to the measurements are large enough to produce the observed deviations. For example, with strong electrolytes $(1 - \alpha)$ is small, and a small error in determining the value of α would produce a considerable change in K .

(b) The method of calculating α is not accurate, since it is assumed that the ionic velocities are independent of the solution concentration. This is certainly not so in strong electrolytes, but the experimental evidence shows that the ionic mobilities approach limiting values at great dilution, and may be taken as constant over a small range.

(c) The formation of complex ions will cause a divergence, since in the ordinary theory it is assumed that only simple ions exist in the solution. There is no evidence, however, of the existence of complex ions in solutions such as potassium chloride.

(d) It may be that ionisation is complete, in which case Ostwald's dilution formula cannot hold, since $(1 - \alpha)$ would be zero, even if C were not zero.

(e) The mass action law may not be applicable to electrolytic ionisation. Arrhenius † suggested that K is a function of the total ionic concentration, and that Ostwald's law was not strictly correct for any actual substance, but in the case of weakly dissociated acids and bases the error, owing to the small ionic concentration, falls within the limits of experimental error.

142. Anomaly of strong electrolytes.—Direct evidence for the view that the mass action law is obeyed by strong electrolytes, even at very great dilution, seems to be of a very uncertain character. For example, the results for potassium chloride lead us to suppose that the law gives a constant value of K at concentrations below 0.0001 normal, but that at a concentration of 0.0005 normal, the value of K has already increased by

* See Partington, *Jour. Chem. Soc.*, 117, 1158 (1910).

† *Zeits. phys. Chem.*, 37, 490 (1901).

100 per cent. The presence of very considerable disturbing influences must therefore be admitted, even at such great dilutions, and there does not appear to be any reason why these influences should disappear at a concentration 0.0001 normal. If, however, we suppose that the strong electrolytes are completely dissociated in dilute solutions, then the changes in conductivity must be attributed to variations in the ionic mobilities, rather than to changes in the ionic concentrations. It must be emphasised that the variation of the conductivity with concentration of weak electrolytes is still explained by the unmodified Arrhenius theory, in which no account is taken of possible changes in the ionic mobilities.

Assuming complete dissociation, the disturbing influences may be attributed to the electrical charges on the ions, and to the effect that they produce on the ionic mobilities. We should expect these influences to persist, even at the greatest dilutions, and the theory of Arrhenius must be modified therefore, so as to take them into account. Thus, for any electrolyte in any solvent, the change in conductivity with concentration is to be attributed to two causes, in part to changes in the mobilities of the ions, and in part to a decrease in their number, resulting from their combination to form neutral molecules.

143. Complete dissociation.—The view that the so-called strong, or strongly dissociated, electrolytes are completely dissociated is not a new one. It has been proposed in particular by Sutherland.* He suggested that ionisation was complete at all strengths, and that account should be taken of the dielectric constant of the solvent and of the ions. He assumed a resistance, which the ions offer to one another's motion because of their forming with the solvent, through their electric action on one another, a medium which offers a special viscous resistance to the motion of each individual ion. This is a new type of viscosity and is of electrical origin. But the charge on each ion causes electric induction through the surrounding solution, and within this is associated a second new type of viscosity, also of electrical origin. These resistances, together with the ordinary viscosity of the solution, give three resistances to ionic motion. When their sum was equated to the electrical accelerating force, a formula for the molecular conductivity was obtained, which was found to be in harmony with the experimental results, obtained with non-aqueous and aqueous solutions, both at ordinary and

* *Phil. Mag.*, 3, 161 (1902); 12, 1 (1906).

at high temperatures. These hypotheses seem somewhat speculative, and the view is not one which is generally accepted.

The supposition, that an electrolyte is completely dissociated, eliminates the long outstanding difficulty of the lack of agreement between the observed freezing-point temperature variation and the mass action law, for the latter clearly does not now come into the matter at all. On the other hand, at first sight, an equally important new difficulty is raised by the existence of a variation in the molecular conductivity with concentration, for this can now no longer be ascribed to incomplete dissociation. However, the interionic forces in a completely dissociated electrolyte may be expected to produce an effect upon the conductivity, as well as upon the osmotic pressure.

144. Ghosh's theory.—In a series of articles Ghosh* advanced a theory of electrolytic solutions on the assumption that all ions, having a kinetic energy above a certain critical value, are effective in transmitting the current through a solution. In determining the fraction of the ions having a velocity above a given value, he assumed, without justification, Maxwell's law for the velocity distribution. A weakness of his theory was that it did not account for those properties of electrolytes which depend upon the nature of the electrolyte itself.

Assuming complete ionisation, he expressed the conductance as a function of the concentration by means of the equation,

$$\log \Lambda = \log \Lambda_0 - \frac{\beta C^{\frac{1}{3}}}{DT},$$

where

$$\beta = \frac{Ne_0^2(2N)^{\frac{1}{3}}}{2.3026mR},$$

and N is Avogadro's number, R , the gas constant, m , a factor depending upon the number of ions produced from a single neutral molecule and the number of charges associated with a single ion, as well as upon the manner of distribution of these ions in the solvent medium, e_0 , the electrostatic unit of charge, and D , the dielectric constant of the solvent. His equation reduces to the form,

$$\Lambda_0 - \Lambda = \Lambda C^{\frac{1}{3}},$$

at very low concentrations, which was one of the formulæ employed by Kohlrausch. Ghosh thought that this result best supported his theory. Plotting the experimental values of $\log \Lambda$ against the cube root of the concentration, the experimental points lay

* *Jour. Chem. Soc.*, 113, 449, 627, 777, 790 (1918).

upon a curve concave towards the concentration axis at low concentrations, and convex towards the axis at high concentrations. If Ghosh's equation were applicable, the points should lie upon a straight line. The deviations of the points from a linear relationship was consistent throughout, and could not be accounted for by errors in the original observations.

If it is assumed that Ghosh's theory accounts for the effect of temperature on the conductivity of electrolytes, it is necessary to suppose that β is not a constant, but varies with the temperature. The actual determination of the value of β depends upon the evaluation of the potential of the electric field due to the ions. To calculate this potential, he found it necessary to ascribe to the ions, not only certain definite charges, but also certain definite fixed positions in the medium. Since β is a function of the temperature and the concentration, as well as of the nature of the solvent medium and the dissolved electrolyte, it follows that in order to account for the variation in β , it is necessary to discard the assumption that the ions occupy a fixed position in the medium, independent of the temperature and the concentration. If this assumption is dropped, it obviously becomes impossible to calculate the potential due to the field of the ions in the medium, unless some other hypothesis is made with regard to the distribution of the charges. If the charges do not occupy a fixed position, but a variable position, dependent both upon the temperature and the concentration, it appears that we must necessarily revert to a kinetic interpretation of the state of the ions in the solution. The distribution of the ions, therefore, must be determined according to the kinetic hypothesis, taking into account the influence of the charges upon the distribution of the particles in the medium, and their motion, relative to one another. The application of Maxwell's distribution law to a system of charged particles, and particularly to a system of charged particles subject to restriction as regards their positions relative to one another, appears a doubtful procedure, since, at the best, Maxwell's law of distribution cannot be expected to hold, save in the case of systems free from constraints.

These important objections do not necessarily mean that the whole theory is incorrect, but it cannot be accepted in its present form. The main idea of complete ionisation, however, has been successfully developed by other investigators, particularly by Milner and Debye and Hückel.

145. Milner's theory.—Milner* has shown that in a gaseous mixture containing N positive and N negative ions within a

* *Phil. Mag.*, 23, 551 (1912); 25, 742 (1913).

volume v , the ions will not be distributed at random, but that the ions of *opposite* sign will be, on an average, slightly *nearer* together, and those of *like* sign, on an average, slightly *further* apart than they would be in a purely random distribution. Since there is a deviation from this random distribution, brought about by the action of the interionic forces, there exists for the mixture a *virial* which, for a purely random distribution, would be zero.

Before proceeding further, let us consider what is meant by a virial. Suppose that the co-ordinates of any molecule in a system are x, y, z , and that the components of the force acting upon it, parallel to the three axes, x, y, z , are, respectively, X, Y, Z . Then Clausius* has shown that the mean kinetic energy of the system is

$$-\frac{1}{2}\Sigma\{xX + yY + zZ\},$$

and this quantity is known as the *virial* of the system.

In the case of electrolytic solutions the virial depends only upon the forces acting upon the ions, and not upon the motion of the ions. The forces included in the virial are of two kinds: (1) the mutual forces between the ions themselves, and (2) a force acting upon the mixture of ions, due to the non-random distribution.

Milner defines the virial, \bar{E} , as

$$\bar{E} = \sum \pm \frac{e^2}{r},$$

where e is the ionic charge and r , the distance apart of any pair of ions. The summation is to be extended, with appropriate sign, over every pair of ions which can be formed out of the $2N$ ions within the volume, and then arranged over every possible configuration of the system, due regard being paid to the probability of the occurrence of each configuration. He found that \bar{E} could be expressed in the form,

$$\bar{E} = N\omega h\phi(h), \quad \cdot \quad \cdot \quad \cdot \quad (146)$$

where

$$h = \left(\frac{4\pi}{3} \cdot \frac{2N}{v}\right)^{\frac{1}{3}} \frac{e^2}{\omega}, \quad \cdot \quad \cdot \quad \cdot \quad (147)$$

and

$$\omega = \frac{RT}{N}.$$

N is the number of molecules in a mole, ω , the most probable value, two-thirds, of the average kinetic energy of translation

* *Phil. Mag.*, August (1870).

possessed by an ion, or a molecule, at the temperature T , and $\phi(h)$ is a function of h , theoretically determinate. It will be noted that h is a pure number, being the ratio of the potential to the kinetic energy.

In equation (146) the interionic forces are reckoned positive when repulsive, and \bar{E} is a negative quantity, $\phi(h)$ being always negative. Put $W = -\bar{E}$, and $\phi'(h) = -\phi(h)$; then,

$$W = N\omega h\phi'(h).$$

The value of W is positive, and W may be called the attractive virial. If the volume v contains one mole of the associated ions, then $N = N$, and $\omega = \frac{RT}{N}$, whence

$$W = RTh\phi'(h). \quad . \quad . \quad . \quad (148)$$

We do not know the exact effect on the interionic forces of the water molecules situated between the electrolytic ions; it is doubtless a very complicated one, but it will certainly diminish the forces very considerably. If we assume that the effect is the same as would be produced if the ions were immersed in a continuous medium, say water, of specific inductive capacity D , the same expression (148) for the virial will apply if, in place of the expression (147) for h , we substitute the value,

$$h = \left(\frac{8\pi N}{3v}\right)^{\frac{1}{2}} \frac{e_0^2}{D\omega}. \quad . \quad . \quad . \quad (149)$$

Let C be the concentration in moles per litre, and F , the charge per gram ion of a monovalent ion, then substituting in equation

$$(149), \quad v = \frac{1000}{C}, \quad N = \frac{F}{e_0} \text{ and } \omega = \frac{RTe_0}{F},$$

we obtain
$$h = \frac{1}{10} \left(\frac{8\pi}{3}\right)^{\frac{1}{2}} \frac{e_0^{\frac{3}{2}} F^{\frac{1}{2}}}{DRT} C^{\frac{1}{2}}.$$

Putting $e_0 = 4.77 \times 10^{-10}$ electrostatic units, $F = 9,654 \times 3 \times 10^{10}$ electrostatic units, $R = 8.31 \times 10^7$ ergs per degree Centigrade, $T = 273$ and $D = 87$ at 0°C. ,

$$h = 1.203 C^{\frac{1}{2}}.$$

Given the virial, we can, if we treat the electrolyte as we should a gas, at once obtain the pressure by using Clausius' equation, namely,

$$\text{pressure} \times \text{volume} = \frac{2}{3} (\text{kinetic energy}) - \frac{1}{3} (\text{virial}).$$

Applied to a completely dissociated electrolyte, this relationship gives, since there are two gram ions present in a volume v ,

$$Pv = 2RT - \frac{1}{3}W,$$

$$\text{or} \quad \frac{Pv}{RT} = 2 - \frac{1}{3}h\phi'(h). \quad (150)$$

Now if δT is the lowering of the freezing-point temperature of a solution, containing C moles of solute per litre, then,

$$Pv = \frac{\delta T}{1.858C} \cdot RT,$$

$$\text{or} \quad \frac{Pv}{RT} = \frac{\tau}{1.858},$$

where τ is the molecular depression, *i.e.*, the depression of the freezing-point temperature per mole of solute per litre. This last relationship is practically independent of whether the osmotic pressure obeys the ideal gas laws or not. By combining it with equation (150) we obtain, for the variation of τ with the concentration in a completely dissociated electrolyte,

$$\tau = 1.858\{2 - \frac{1}{3}h\phi'(h)\}.$$

Milner found that the experimental and calculated values of τ for potassium chloride, sodium chloride and ammonium chloride agreed very closely, and that there was a fair agreement for the nitrates of ammonium, sodium, potassium, rubidium, and caesium.

Summarising Milner's extremely important work, he assumed complete dissociation of electrolytes in dilute aqueous solutions, and taking into account the interionic forces, he developed an expression for the depression of the freezing-point temperature which agreed well with experimental results. The theory was not developed so as to apply to the electrical conductance of electrolytic solutions.

146. Debye and Hückel's theory.—Debye and Hückel* have deduced a relationship between the equivalent conductance and the concentration, which is based on two general principles, one, the so-called Boltzmann's principle from the kinetic theory of gases, and the other, known as Poisson's equation, is derived from the law of electrostatics and involves Coulomb's law. They applied these principles, in the first place, to determine the

* *Phys. Zeits.*, 24, 185 (1923).

distribution of the ions of opposite charges around any selected ion, and to evaluate the potential that prevails around the ion in consequence of its own charge, and of the unequal distribution which it produces in the surrounding ions.

Consider an ion at O (Fig. 56), having an electrical charge equal to e . This ion produces in any shell, of volume δv , located between distances r and $r + \delta r$, a potential, ψ , and a density, ρ , of electric charge. Now, if a large number of molecules possess an average kinetic energy, $\frac{3}{2}kT$, and are distributed throughout a region in which there are, at different points, different fields of force, there will be, accordingly, different potentials, and any kind of molecule, in a volume element δv , will acquire a definite potential energy, E . The number of molecules in this volume which possess energy, E , will equal the number of molecules per unit volume, at a place where E is zero, multiplied by the factor $e^{-\frac{E}{kT}}$ and the volume δv , where e is the base of Napierian logarithms.

This result is known as Boltzmann's principle, and k is defined as Boltzmann's constant.

Consider an ion migrating in a solution, and imagine a line of fixed length connected with the ion, in such a way that during the migration of the ion, the direction of this line in space is maintained constant. At the end of the line we imagine an elementary volume. If we consider the ion and its elementary volume for a certain time, we find that sometimes an excess of positive,

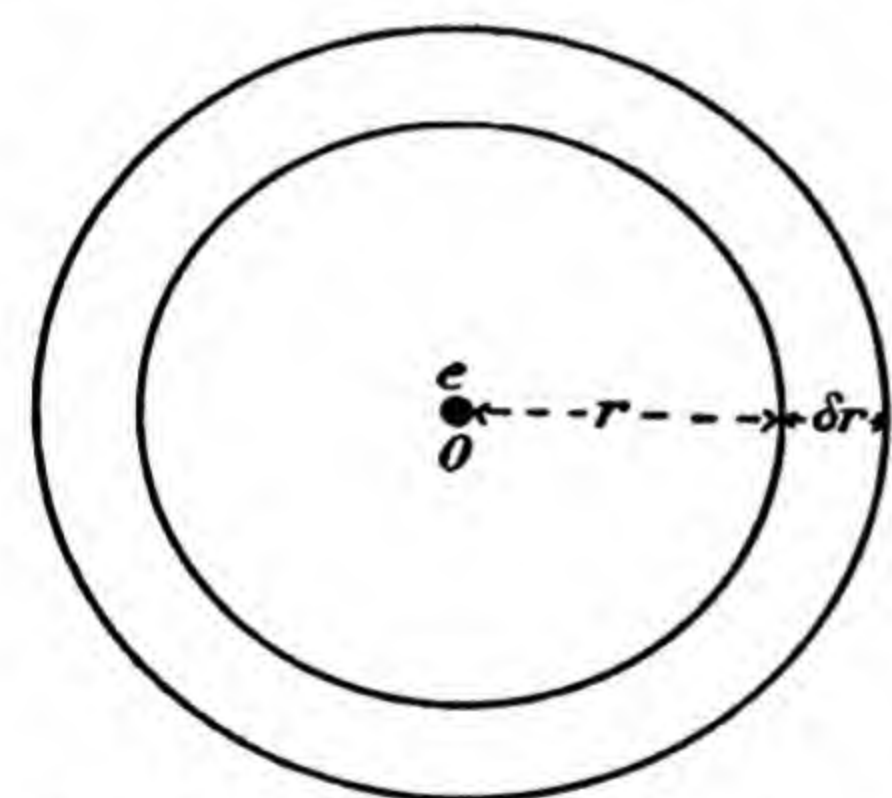


FIG. 56.—The ionic atmosphere.

and sometimes an excess of negative, electrical charge, is contained within the elementary volume, due to the various ions within the solution. Taking the time integral of this charge, and dividing by the whole time of observation, we obtain the mean charge within the element. The density of the electricity within the space surrounding an ion—this space is known as the *ionic atmosphere*—is thus the mean charge divided by the volume, and it is obvious that, as far as the Coulomb forces alone are considered, the electrical density within the ionic atmosphere will be of opposite sign to the charge on the ion. Thus the ionic atmosphere surrounding any selected *positive* ion will contain an excess of *negative* electricity. This will cause an average electrical potential, ψ , and an average electrical density, ρ , to exist at any distance

from the selected ion. If we apply Boltzmann's distribution principle, we have

$$\rho = ne\left(\epsilon^{-\frac{e\psi}{kT}} - \epsilon^{\frac{e\psi}{kT}}\right), \quad (151)$$

where e is the charge on a positive ion, T , the absolute temperature, and n the number of positive ions per cubic centimetre of solution.

Assuming Poisson's equation,*

$$\nabla^2 \psi = -\frac{4\pi\rho}{D}, \quad (152)$$

where D is the dielectric constant of the medium in which the ions are situated.

Hence from equations (151) and (152),

$$\nabla^2 \psi = -\frac{4\pi en}{D}\left(\epsilon^{-\frac{e\psi}{kT}} - \epsilon^{\frac{e\psi}{kT}}\right),$$

or
$$\nabla^2 \psi = \frac{8\pi en}{D} \sinh \frac{e\psi}{kT}.$$

The average potential in the space around the selected ion depends only upon the distance from the ion, and for small values of the potential, ψ , we may write

$$\sinh \frac{e\psi}{kT} = \frac{e\psi}{kT},$$

and thus,
$$\nabla^2 \psi = \frac{8\pi e^2 n \psi}{DkT}.$$

Transforming to polar co-ordinates, we have

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial \psi}{\partial r} = \kappa^2 \psi, \quad (153)$$

where

$$\kappa^2 = \frac{8\pi e^2 n}{DkT},$$

$\frac{1}{\kappa}$ having the dimension of a length, and being known as the *thickness of the ionic atmosphere*. It is a characteristic factor in the theory of Debye and Hückel.

Integrating equation (153) we obtain,

$$\psi = \frac{A\epsilon^{-\kappa r}}{r},$$

* See Appendix I.

where A is a constant, so that if r is small, *i.e.*, if we consider points not far removed from the ion,

$$\psi = \frac{A}{r} - A\kappa,$$

and this expression represents the total potential at a point distant r from an ion. But this potential is made up of two parts, namely, that due to the ion, if there were no surrounding ions, and that arising from the ionic atmosphere, *i.e.*, from the unequal distribution of the positive and negative ions in the surroundings. At infinite dilution the potential at a point will be that due to the ion alone, $\frac{e}{Dr}$, so that $A = \frac{e}{D}$, and thus the potential at points very close to the ion, arising from the existence of the ionic atmosphere, is given by

$$\psi = -A\kappa = \frac{-e\kappa}{D}.$$

In other words, the potential of the ion itself resulting from the ionic atmosphere is $\frac{-e\kappa}{D}$.

If the electrolyte is not a simple one, then,

$$\kappa^2 = \frac{4\pi}{DkT} \sum n_i e_i^2, \quad . \quad . \quad . \quad (154)$$

n_i being the number of the ions of the i th sort.

Debye and Hückel assumed that strong electrolytes in dilute solutions are completely dissociated, and they attributed the variations of the conductance with concentration to changes in the ionic mobilities, and not to any change in the fraction of the number of molecules dissociated. The velocity of an ion, as it moves through a liquid, depends upon the accelerating forces, produced by electrical forces and the frictional, or retarding, forces which always act upon a body moving through a viscous medium.

An ion at rest possesses a symmetrical ionic atmosphere, but the symmetry will be destroyed as soon as the ion moves. Thus, when an external electric field is applied to an electrolytic solution an ion moves, say to the right, and during its motion it will have to build up, as it were, an electrical charge density to the right, but to the left of the ion the electrical charge density is too large, and will have to decrease. If the ionic atmosphere were created, or changed in value, instantaneously, the central symmetry would exist, even during the ionic motion, but this is not the case. Since the charge density in the ionic atmosphere

For steady ionic motion through the solvent the sum of the accelerating electrical forces acting upon an ion must be equal to the total frictional, or retarding, forces and thus,

$$e_i X - \frac{e_i^2 \kappa \zeta}{6DkT} u_i = \zeta_i u_i + e_i X b_i \kappa,$$

or

$$u_i = \frac{e_i X}{\zeta_i} \cdot \frac{1 - b_i \kappa}{1 + \frac{\zeta}{\zeta_i} \cdot \frac{e_i^2 \kappa}{6DkT}},$$

$$\text{i.e., } u_i = \frac{e_i X}{\zeta_i} \left[1 - b_i \kappa - \frac{\zeta}{\zeta_i} \cdot \frac{e_i^2 \kappa}{6DkT} \right], \text{ approximately.} \quad (156)$$

At infinite dilution $\kappa = 0$, and

$$(u_i)_0 = \frac{e_i X}{\zeta_i}, \quad \text{where } 6\pi\eta b_i = \zeta_i.$$

Since the equivalent conductance, Λ , is proportional to the ionic velocity, we see that the change in Λ , produced by changes in concentration, is proportional to κ . But κ , the reciprocal of the radius of the ionic atmosphere, is proportional to the square root of the concentration, equation (154), and therefore this theory of interionic attraction leads to Kohlrausch's formula **section (140)** for the relation between equivalent conductance and concentration.

Now the specific conductivity, σ , of an electrolytic solution is equal to $\frac{1}{X} \sum n_i e_i u_i$, and so, from equation (156),

$$\sigma = \sum \frac{n_i e_i^2}{\zeta_i} - \left[\sum \frac{n_i e_i^2 b_i}{\zeta_i} + \sum \frac{n_i e_i^4}{6DkT} \cdot \frac{\zeta}{\zeta_i^2} \right] \kappa.$$

$$\text{At infinite dilution, } \sigma_0 = \sum \frac{n_i e_i^2}{\zeta_i}.$$

Thus, using the values of ζ and κ , as given in equations (155) and (154), respectively, we have

$$\frac{\sigma_0 - \sigma}{\sigma_0} = \sqrt{\frac{4\pi}{DkT} \sum n_i e_i^2} \left[\frac{\sum \frac{n_i e_i^2 b_i}{\zeta_i}}{\sum \frac{n_i e_i^2}{\zeta_i}} + \frac{\sum n_i e_i^2 \zeta_i}{\sum n_i e_i^2} \cdot \frac{\sum \frac{n_i e_i^4}{6DkT \zeta_i^2}}{\sum \frac{n_i e_i^2}{\zeta_i}} \right].$$

Suppose that every molecule of solute, when in solution, dissociates into z_1, z_2 , etc., ions of valencies ν_1, ν_2 , etc., then,

$$\frac{\sigma_0 - \sigma}{\sigma} = \sqrt{\frac{4\pi e_0^2}{DkT}} \cdot zn \left[bw_2 + \frac{e_0^2}{6DkT} w_1 \right], \quad (157)$$

where $\pm e_0$ is the charge on a univalent ion, n , the number of molecules of solute per c.c., and

$$z = \sum z_1, z_2, \text{ etc.},$$

$$w_1 = \frac{\sum z_1 \nu_1^2 \zeta_1}{\sqrt{z \sum z_1 \nu_1^2}} \cdot \frac{\sum \frac{z_1 \nu_1^4}{\zeta_1^2}}{\sum \frac{z_1 \nu_1^2}{\zeta_1}},$$

$$w_2 = \sqrt{\frac{\sum z_1 \nu_1^2}{z}},$$

and

$$b = \frac{\sum \frac{z_1 \nu_1^2 b_1}{\zeta_1}}{\sum \frac{z_1 \nu_1^2}{\zeta_1}}.$$

For example, in the case of a uni-univalent electrolyte, such as potassium chloride, $z_1 = z_2 = 1$ and $\nu_1 = \nu_2 = 1$, so that

$$w_1 = \frac{\zeta_1 + \zeta_2}{2} \cdot \frac{\frac{1}{\zeta_1^2} + \frac{1}{\zeta_2^2}}{\frac{1}{\zeta_1} + \frac{1}{\zeta_2}} = \frac{\zeta_1^2 + \zeta_2^2}{2\zeta_1\zeta_2},$$

$$w_2 = \sqrt{1} = 1,$$

$$\text{and } b = \frac{\frac{b_1}{\zeta_1} + \frac{b_2}{\zeta_2}}{\frac{1}{\zeta_1} + \frac{1}{\zeta_2}} = \frac{b_1\zeta_2 + b_2\zeta_1}{\zeta_1 + \zeta_2}.$$

Now the equivalent conductance, Λ , is given by $\Lambda = \frac{1000 \sigma}{C}$,

where C is the concentration in moles per litre, and $n = \frac{NC}{1000}$, N

being the number of molecules per mole. Hence, for aqueous solutions of uni-univalent electrolytes, at 18° C., we have, on substituting the values of the various constants in equation (157),

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[0.233 \times 10^8 \frac{b_1\zeta_2 + b_2\zeta_1}{\zeta_1 + \zeta_2} + 0.273 \frac{\zeta_1^2 + \zeta_2^2}{2\zeta_1\zeta_2} \right] \sqrt{2C},$$

and we thus obtain the relation between the equivalent conductivity and the concentration of an electrolyte, found empirically by Kohlrausch. The calculated and experimentally determined

values of the equivalent conductivity of potassium chloride are given in Table LXV.

TABLE LXV.

CALCULATED AND EXPERIMENTALLY DETERMINED VALUES OF THE EQUIVALENT CONDUCTIVITY OF POTASSIUM CHLORIDE.

$2C.$	$\sqrt{2C.}$	Λ (calculated).	Λ (observed).	Difference.
0.0002N	0.014142	129.09	129.07	— .02
0.0004N	0.020000	128.75	128.77	+ .02
0.0010N	0.031623	128.08	128.11	+ .03
0.0020N	0.044721	127.34	127.34	.00
0.0040N	0.063246	126.32	126.31	— .01
0.0100N	0.100000	124.39	124.41	+ .02
0.0200N	0.14142	122.36	122.43	+ .07
0.0400N	0.20000	119.75	119.96	+ .21
0.1000N	0.31623	115.51	115.75	+ .24

There is close agreement between the calculated and observed values of the equivalent conductance at different concentrations. Debye and Hückel have made a comprehensive survey of conductivity data for dilute solutions, and have shown that they are in fair agreement with their theory. Similar comparisons for non-aqueous solvents are more difficult, as the experimental data are far less homogeneous and complete, but Hartley and Frazer* have shown that the relationship between equivalent conductance and concentration does hold for many uni-univalent salts in methyl alcohol, up to concentrations of 0.002 normal. Many other investigators† have also found that there is very close agreement between the experimental values of the equivalent conductance and those calculated on Debye and Hückel's theory, and that this theory accounts satisfactorily for the conductivity of completely dissociated electrolytes in different solvents.

Since the potential of an ion, due to its ionic atmosphere, is $-\frac{e\kappa}{D}$, it follows that, if ν_i is the valency of any particular ion and e_0 , the charge on a positive univalent ion, the increase, δE_i , in its energy, caused by its removal from its ionic atmosphere, is given by

$$\delta E_i = \frac{\nu_i^2 e_0^2 \kappa}{D}.$$

* *Proc. Roy. Soc., A*, 109, 351 (1925).

† See *Trans. Farad. Soc.*, 23, 333 (1927).

If all the ions in any given solution are removed from the influence of their ionic atmospheres, the energy increase is $\frac{1}{2}\Sigma\delta E_i$. The factor $\frac{1}{2}$ comes in, otherwise the effect of separating any given pair of ions would be counted twice. In view of the additivity of the energy effects, we may distribute this energy increase among the different kinds of ions present. Thus, the energy-increase, ΔE_i , attending the removal of N molecules constituting one mole of any particular kind of ion, of valence ν_i , is given by

$$\Delta E_i = \frac{Ne_0^2\nu_i^2\kappa}{2D}.$$

Substituting the value of κ from equation (154),

$$\Delta E_i = \frac{Ne_0^3\nu_i^2\sqrt{\pi}\sqrt{\Sigma n_i\nu_i^2}}{(D^3kT)^{\frac{1}{2}}},$$

and for a concentration of C moles per c.c.,

$$\Delta E_i = \frac{A\nu_i^2\sqrt{\Sigma C_i\nu_i^2}}{\sqrt{D^3T}},$$

where A is equal to $e_0^3N^2\sqrt{\frac{\pi}{R}}$, R being written for Nk . In the general case, where n_a moles of the ion A, n_b moles of the ion B, etc., are present in the solution, the difference between their energy contents in the infinitely dilute and in the more concentrated solution is given by

$$\Sigma(n_i\Delta E_i) = \frac{A\Sigma(n_i\nu_i^2) \cdot \sqrt{\Sigma C_i\nu_i^2}}{\sqrt{D^3T}}. \quad (158)$$

Milner had previously determined the energy change, corresponding to the inter-ionic attraction, in the case of a single salt with ions of equal valence, and his expression was approximately two-thirds of that given in equation (158). This difference has now been explained. Adams* has pointed out that the quantity obtained by Debye and Hückel is the free energy of *transfer* of ions from a given solution to a very dilute solution in which the electrical forces are negligible, and is equal to the *free energy* change at *constant pressure*, not the change in the *total internal energy*. Only if the dielectric constant is independent of temperature are these two thermodynamic functions equal. Milner, on the other hand, calculated the work done in separating the ions in a given solution to an infinite distance from one another. This

* *Jour. Amer. Chem. Soc.*, 48, 621 (1926).

is equivalent to a change in the *work content*, or a change in Helmholtz's *free energy*, and this maximum electrical work is two-thirds of the free energy change at constant pressure, if the inverse square law of force is assumed. Thus, the discrepancy between the two results is explained.

To derive an expression for the osmotic pressure, we may consider the virial equation of a gas, namely,

$$Pv = \frac{1}{3}mnu^2 - \frac{1}{3}\Sigma(\mathbf{f} \cdot r), \quad (159)$$

where $\Sigma(\mathbf{f} \cdot r)$ is the virial, and denotes the sum, for all the pairs of the n molecules in a volume v of gas, of the products of the force \mathbf{f} between the molecules of each pair and their distance r apart, m , the mass of each molecule, u its kinetic velocity, and p , the gas pressure. If the force function is of the form, $\mathbf{f} = \frac{X}{r^2}$, where X is the force acting between two molecules at unit distance apart, then the virial is evidently the difference between the energy which the molecules possess in a perfect gas, and that in the actual gas. If we assume that the virial equation is applicable also to solutions, the osmotic pressure replacing the gas pressure, we can at once derive an expression for the osmotic pressure, P . Thus, if the solution contains one mole of positive ions and one mole of negative ions in the volume v , and each ion is of valence $\pm \nu$, we have, from equation (158),

$$2\Delta E = \frac{2A\nu^2\sqrt{2C\nu^2}}{\sqrt{D^3T}},$$

and thus,

$$Pv = 2RT - \frac{2A\nu^2\sqrt{2C\nu^2}}{3\sqrt{D^3T}},$$

since $\Sigma(\mathbf{f} \cdot r) = 2\Delta E$, and $\frac{1}{3}mnu^2 = 2RT$. Putting $\frac{1}{v} = C$, we have

$$P = 2CRT - \frac{2AC\nu^2\sqrt{2C\nu^2}}{3\sqrt{D^3T}}. \quad (160)$$

From this equation we may derive an expression for the freezing-point temperature depression, if we assume proportionality between freezing-point temperature depression and osmotic pressure. Debye and Hückel made an extensive study of existing freezing-point data and showed, graphically, that for ionic

strength * up to about 0.03N, uni-univalent, uni-bivalent and bi-bivalent salts yield freezing-point temperatures which agree with those calculated by means of equation (160).

Other striking confirmatory evidence which supports Debye and Hückel's theory is that values of the mean apparent radius of the various ions, calculated by means of equation (157), agree well with those determined in other ways.† The values approximate more closely in the case of ions such as sodium, barium, chloride, *etc.*, where the electron structure is of the noble gas type.

Having considered the evidence which supports Debye and Hückel's theory of complete dissociation, at low concentrations, and the interionic theory, we now pass on to consider evidence which indicates that in many cases the theory must be modified to some extent. The mathematical theory is not yet in a final form, even for dilute solutions, since there is still uncertainty as to the exactness with which Stokes's law is obeyed, the effect of the intense electrical fields produced locally by the electrical attractions between the ions, and the way in which the dielectric constant varies with the concentration of the electrolyte. Nevertheless, in its present form, it does give support to the belief that strong electrolytes are completely dissociated in dilute solution, and that the interionic forces are responsible for the changes in their properties which occur with dilution.

Even in dilute salt solutions, however, specific chemical interaction between the ions may be of importance, as well as the normal electrical attraction which exists between them. It is true that in dilute aqueous solutions there is a surprisingly close agreement between the behaviour of salts of the same valency type, although mercury salts form a striking exception, but when we pass to non-aqueous solvents with a lower dielectric constant than that of water, the purely physical aspect of the ionic relationship becomes more limited in its application, while the specific interaction of the ions begins to play a more important part. For example, with water the slopes of the equivalent conductance—concentration curves for the uni-univalent salts are practically the same, but with methyl alcohol the results are far less regular; the curves for most nitrates have a different slope from that for the chlorides, and the conductance values for silver nitrate fall

* The ionic strength of a solution is obtained by multiplying the concentration of each ion by the square of that ion's valence number, summing all these products, and dividing the result by two.

† See Hückel, *Phys. Zeits.*, 26, 93 (1925); Harned and Akerlöf, *ibid.*, 27, 411 (1926); Harned, *Jour. Amer. Chem. Soc.*, 48, 326 (1926).

more rapidly, as the concentration is increased, than those for any other salt. These differences are too great to be accounted for by differences in the sizes, or relative mobilities, of the ions, and they indicate, in some cases, incomplete dissociation due to interaction between the ions. With divalent ions the discrepancies in non-aqueous solvents are still more marked. With methyl alcohol, the calcium chloride and the perchlorate curves are normal in slope, while calcium nitrate behaves like a weak electrolyte; on the other hand, the zinc perchlorate and nitrate curves are normal, while the curve for chloride is abnormal. Whether this is due to the formation of complex ions or molecules is not yet known definitely, but it is evident that in dilute non-aqueous solutions the specific interactions of the ions—in fact their chemical affinities—may dominate the situation.

Bjerrum * has come to the conclusion that certain electrolytes, among them potassium nitrate and the iodates of potassium and sodium, cannot be completely dissociated. His argument is that a certain proportion of the ions will form pairs which will act osmotically as single molecules if one, or both, of the ions has a radius smaller than a critical value. Under these conditions the ions will approach so near to each other that the attraction of a positive ion for a negative ion will be, for short periods, greater than the combined attractions of all the surrounding positive ions on the negative ion. According to this author, it is necessary to assume very small, or even negative, values for the ionic diameters in the Debye and Hückel equation, if correction is to be made for this association. Mueller † claims, however, that if a more rigorous mathematical deduction is made of the factors determining the inter-ionic forces, Debye and Hückel's theory will account for small ions without necessarily assuming association. MacInnes and Cowperthwaites' ‡ computations favour Bjerrum's conclusions, although the latter call for larger degrees of association than those found by the former experimenters.

McBain and Rysselberge's results § for complex ions indicate that the real value of α , the degree of ionisation, must be less than unity, and that the numerical values of the coefficients occurring in equation (157) must be altered accordingly. Recently Nernst || has argued that some strong electrolytes must be incompletely dissociated, because the heats of dilution are of opposite sign to that predicted solely from the interionic attraction theory.

* *Kgl. Danske. Viden. Sels.*, 7, 9, 2 (1926).

† *Phys. Rev.*, 29, 216 (1927).

‡ *Trans. Farad. Soc.*, 23, 400 (1927).

§ *Jour. Amer. Chem. Soc.*, 50, 3009 (1928).

|| *Zeits. Elektroc.*, 33, 428 (1927).

He suggests a degree of dissociation for strong electrolytes which agrees with the mass law. His hypothesis, however, is not yet completely developed.

Fajans * deduced from optical measurements that neutral molecules and complex ions are present in solutions of strong electrolytes. Thus, from refractivity experiments with a 5 molal solution, the formation of undissociated molecules was found to be, approximately, a few per cent., and for a concentration 0.01 molal, of the order $\frac{1}{100}$ per cent. The numbers are small, but if they are real, they cannot be looked upon as supporting complete dissociation experimentally, since with hydrochloric acid, for which there is general agreement as regards the existence of undissociated molecules in solution, the concentration of the undissociated hydrochloric acid, obtained from partial pressure measurements, was smaller still. Fajans calculated that in a 5 molal solution of this acid, 6.3 per cent. of the molecules are undissociated, and in a 0.01 molal solution the percentage is 0.012. Ebert, † from vapour pressure measurements, showed that in a 0.01 molal solution of hydrochloric acid, the concentration of the undissociated moles was 5.9×10^{-12} .

For equi-concentrated solutions of different salts possessing a common ion, the product of the equivalent conductance and the transference number of the common ion should be the same, if the salts are completely dissociated. MacInnes and Cowperthwaite ‡ have shown from this result that even if alkali chlorides are assumed to be completely dissociated in a 0.1 normal solution, the nitrates of sodium, potassium and silver must be incompletely dissociated, or at least, their ions must be partly paired, or associated, in the manner supposed by Bjerrum.

The square root relationship between equivalent conductance and concentration is only an approximation, applicable at great dilutions. At finite concentrations, deviations from this law must occur, even if it is true at very small concentrations. The deviations depend upon the individual properties of the ions, such as their dimensions, as well as upon the variation of the viscosity of the solution with concentration, and particularly upon the deviations from Coulomb's law, which probably occur when the distance between two ions becomes small, as it does, in association, or hydration. In spite of the validity of the square root law for electrolytic solutions in the higher alcohols, abnormally large values of the ionic radius are found in these solutions, and, therefore, conformity to this square root relationship is no

* *Trans. Farad. Soc.*, 23, 357 (1927).

† *Naturwiss.*, 13, 393 (1925).

‡ *Loc. cit.*

guarantee that the variation of conductivity with concentration will be in accordance with Debye and Hückel's equation.

Finally, Nernst* has shown that, if the greater decrease in equivalent conductance with increasing concentration of certain electrolytes in water, compared with that of potassium chloride and potassium bromide, be assumed to be due to incomplete dissociation, values of the degree of dissociation are obtained which are in approximate agreement with those calculated from the freezing-point temperature depressions, although the effect of interionic attraction is taken into account in calculating these depressions.

There is still the effect of the variation of the dielectric constant with concentration to be considered, but this will be discussed later. On the whole, however, while the theory of complete ionisation has met with such marked success, it is not applicable to all electrolytic solutions. Although the conception of a strong electrolyte is a modern one, the existence of strong and weak acids has been familiar for many years, and their properties had already been interpreted in many other ways, before the strength of an acid was finally correlated with its electrical conductivity in dilute solutions. The theory of complete ionisation receives its most serious challenge from the existence of weak acids which obey Ostwald's dilution law. In addition, as pointed out in **section (42)**, Ferguson and Vogel have shown that, in general, even in dilute solutions, the equivalent conductance of strong electrolytes is not strictly proportional to the square root of the concentration.

147. Onsager's Theory.—Debye and Hückel assumed that the total electric force acting upon an ion was equal to the sum of the external electric force and the additional electric force due to the non-symmetry of the ionic atmosphere, this dissymmetry arising from the movement of the ion. Onsager† argued that an ion which is moved with a constant velocity in a solution is not, strictly speaking, the same as a real ion, which, besides its mean motion in one direction, also possesses a Brownian movement. This irregular motion can indeed be expected to have an effect on the dissymmetry of the ionic atmosphere. If we suppose the ion constrained to follow a given path, thus suppressing its Brownian motion, we shall always obtain too high a value for the resistance to motion, acting upon it as it moves through the liquid, and, also, a further correction must be introduced to allow for the migration of the ions forming

* *Loc. cit.*

† *Phys. Zeits.*, 27, 388 (1926); *ibid.*, 28, 277 (1927); *Trans. Farad. Soc.*, 23, 341 (1927).

the ionic atmosphere. In the case where the mobilities of the ions of a uni-univalent electrolyte are equal, the correction term is $2 - \sqrt{2}$, so that Debye and Hückel's equation, which may be written in the form,*

$$\Lambda_0 - \Lambda = \Lambda_0(K_1 w_1 + K_2 b) \sqrt{2C},$$

becomes

$$\Lambda_0 - \Lambda = \Lambda_0[K_1(2 - \sqrt{2}) + K_2 b] \sqrt{2C}.$$

For potassium chloride at 18° C., $\Lambda_0 = 129.9$, and the Debye and Hückel expression leads to the equation,

$$\Lambda_0 - \Lambda = 0.547 \sqrt{2C},$$

whereas Onsager's gives

$$\Lambda_0 - \Lambda = 0.433 \sqrt{2C},$$

as against the experimentally observed value $0.461 \sqrt{2C}$. The validity of Onsager's formula is restricted to the simple binary electrolytes, and even then it is only true for very dilute solutions, but on the whole, there is close agreement between the experimental values of the equivalent conductance and those calculated from his equation for uni-univalent and for uni-bivalent electrolytes in water.

Other theories of solutions, dealing more particularly with the relation between their osmotic pressure and the relative lowering of their vapour pressure, have been put forward by Porter † and Sackur.‡

148. The dielectric constant of electrolytic solutions.

—We have seen that the dielectric constant of an electrolytic solution plays an important part in modern electrolytic theories and, accordingly, we now consider, in some detail, the manner in which this function depends upon the concentration of the solution.

If a molecule of any substance is subjected to the action of an electric force, the molecule becomes polarised, its electric moment for small values of the electric force being proportional to this force. It can be shown that

$$\frac{D - 1}{D + 2} \cdot \frac{M}{\rho} = \frac{4}{3} \pi N a,$$

where M is the molecular weight of the substance, ρ , the density, N , Avogadro's constant, and a , a constant, which, for some

* See section 42.

† *Proc. Roy. Soc.*, A, 79, 519 (1907); 80, 427 (1908).

‡ *Lehrbuch der Thermochemie und Thermodynamik*, p. 200.

substances, changes with the temperature. In these cases the dielectric constant changes with temperature, even if the density remains the same.

Formerly, it was supposed that under the influence of an applied electric force every molecule was distorted to a certain extent. As the charges building up a molecule are partly positive, and partly negative, and these charges are displaced in opposite directions by the electric field, the result of such a distortion will be the appearance of an electric moment, the average value of which is independent of the temperature.

Further, it seems more than probable that, in general, a molecule may show an electrical dissymmetry which results in the existence of a residual electrical moment. This moment, too, can be oriented with the help of the electric field and, therefore, owing to this orientation effect, these molecules will contribute to the polarisation. As the orientation effect will depend upon the intensity of the molecular collisions, we should expect that the polarisability would depend upon the temperature, decreasing as the temperature falls. In practice, it has been shown definitely that N_2O_2 and C_6H_6 are symmetrical molecules, whereas NH_3 and H_2O are polar, their electric moments having very appreciable values. The order of magnitude of this moment is always 10^{-18} , as expected, since the product of the electronic charge and a length, comparable with the molecular diameter, is of this order.

If a gas, consisting of molecules which are non-symmetrical and cannot be distorted in any way, be placed in an electric field, and the field strength then increased, it is to be expected that the mean molecular moment would increase as more and more molecules are oriented by the field. Finally, however, the field might become so strong that all of the molecules would have their moments lined up, as it were, in the direction of the field, and there would be no further increase in the mean moment. The same phenomena might be described by saying that the dielectric constant begins to decrease when the field is made very strong, the final value being unity, and that the beginning of this effect is the commencement of saturation. When saturation sets in, the function a is no longer a constant but decreases, and therefore, the dielectric constant must also decrease.

Direct measurements of the change in the dielectric constant in strong fields, made by Ratnowski * and by Herweg,† seem to have proved the existence of this saturation effect. The dielectric

* *Verhandl. deut. physik. Ges.*, 15, 497 (1913).

† *Phys. Zeits.*, 3, 36 (1920); Herweg and Potzsch, *ibid.*, 8, 1 (1922).

constant was found to decrease slightly when a strong electric field, of the order 10^5 volts per centimetre, was superimposed upon the small measuring field.

Values of the dielectric constant for electrolytic solutions, determined by Walden,* show that for small concentrations this constant has a lower value than that of the pure solvent. Now at molecular distances from the ions we have to deal with very large electrical fields of the order 10^6 volts per centimetre, and thus the ions set up electrical saturation in the neighbouring molecules of a solvent, such as water. If, furthermore, we consider only very dilute solutions, it will not be necessary to take into account the mutual interaction between the ions. Within the neighbourhood of the ions, then, the solvent molecules will assume positions with their moments parallel to the radial field.

When a small measuring field is applied between two parallel planes in the electrolyte, since the field due to the ions will have oriented the neighbouring solvent molecules, the small measuring field cannot orient them as much as it can in pure water, and thus we may look upon the saturation effect, produced by the ions, as the equivalent of making holes, as it were, in the solvent around each ion, the radii of the holes depending upon the distance to which the saturation effect extends.

From these considerations we should expect the dielectric constant of a salt solution to be less than that of the pure solvent. Thus Sack † has shown that for very dilute solutions the dielectric constant decreases linearly with concentration. He used solutions of salts of various types, including potassium chloride, barium chloride, and copper sulphate. The ions formed from these salts carry different charges, and this fact was found to affect the dielectric behaviour of the electrolyte. His results show that

$$D = D_0(1 - bC),$$

where D is the dielectric constant of the solution, D_0 , that of the pure solvent, C , the concentration, and b , a constant which is characteristic of the kind of ions.

Now Sack recognised that if the effect is a saturation one, the value of b should depend only upon the charge on the ions, and not upon other physical characteristics, at least to a first approximation. He found that the value of b could be determined by a summation process, extended over all the different kinds of ions, and that for a single ion, its value should be proportional

* *Zeits. phys. Chem.*, 110, 44 (1924); *ibid.*, 116, 261 (1925).

† *Phys. Zeits.*, 27, 206 (1926); 28, 199 (1927).

to the charge³ or to valency³. He verified this conclusion from his experiments on different salts.

Walden, Ulich and Werner,* by means of a high frequency resonance apparatus, measured the dielectric constants of a large number of liquids, and obtained curves, plotting the cube root of the concentrations against the dielectric constants. In all cases they found a lowering of the dielectric constant, proportional to the concentration at low concentrations, but there was a minimum value beyond which the dielectric constant increased with concentration. The rising part of the curve varied with different solutions, but with aqueous solutions, on account of the limited solubility of the salts employed, only the descending part of the curve was realised. The slope of the downward part of the curve, as well as the position of the minimum value, varied with the dielectric constant of the solvent.

Walden and Werner,† Hellmann and Zahn,‡ Nayder,§ Partington and Rule || and many others have investigated this effect, and the reader is advised to consult the paper by Blüh ¶ for a full description of recent work on dielectric constants. For example, Hellmann and Zahn found that electrolytes were divisible into two groups: those, such as hydrochloric acid, which even at high concentrations show little lowering of the dielectric constant, and those, like copper sulphate, which show the effect even at very low concentrations.

Hückel ** found that the variation of the dielectric constant with changing salt concentration makes the self potential of the ion, which was neglected in the original Debye and Hückel theory for the case of dilute solutions, appear as a significant factor in the domain of concentrated solutions.

When hydration, electrical effects due to the ions, ionic association, change in the dielectric constant, *etc.*, unite, as they certainly do, in influencing the behaviour of ions, any theory which can explain the observations on the basis of one, or a few, of these influences cannot possibly be trusted as a sound solution of the problem. It should not be overlooked that strong salt solutions also exert a very remarkable effect on the molecules which have no net electrical charge.

In solvent media which possess smaller dielectric constants than that of water, the increased inter-ionic electrical forces will

* *Zeits. phys. Chem.*, 116, 261 (1925).

† *Ibid.*, 124, 405 (1926).

‡ *Acad. Pol. Sci. et Lettres Bull.* No. 7(a), 247 (1925).

§ *Phil. Mag.*, 1, 1035 (1926).

¶ *Phys. Zeits.*, 27, 226 (1926).

† *Phys. Zeits.*, 27, 636 (1926).

** *Ibid.*, 26, 93 (1925).

cause larger deviations from the ideal laws of solution. We must expect the limit of the application of Debye and Hückel's theory for such solutions to be at a still lower concentration than for aqueous solutions. The tendency of ions to associate, which of course increases with increasing electrical charge and with decreasing ionic size, will be more marked for such solvents. Substances which are practically strong electrolytes in water may prove to be weak, or incompletely dissociating substances, in non-aqueous solvents.

149. The Wien effect.—Under ordinary conditions the conductivity of an electrolytic solution is independent of the applied potential used in measuring it, but Wien,* measuring the conductance of solutions of sodium chloride, sulphuric acid, beryllium sulphate and calcium ferrocyanide, at high current frequencies, and at voltages up to 80 kilo-volts per cm., found that in all cases the value of the equivalent conductivity depends upon the potential and increases with the applied field strength. This "potential effect," or *Wien effect*, increases rapidly with the valency of the ions. With intense fields, changes of the conductivity value exceeding 60 per cent. were observed, and this potential effect at first increases linearly, approximately, with the field, but with very strong fields the conductivity tends to a constant value—the limiting value. The effect depends upon the concentration, in that the initial rise of the conductivity is steeper, the more dilute the solution. In very dilute solutions the "limiting value" is attained with comparatively low fields. With concentrated solutions the rise is slower, but continuous, so that the limiting value is higher than with dilute solutions.

Later, Wien† worked with weaker fields and obtained the following results:—

(a) The potential effect, $\Delta\Lambda$, in weaker fields may be represented, for all solutions investigated, by the expression

$$\Delta\Lambda = AX^2(1 - BX^2),$$

where $\Delta\Lambda$ is the change in the equivalent conductance, A and B , constants, and X , the external field in volts per cm. which produces the change $\Delta\Lambda$.

(b) A is, approximately, proportional to the square of the product of the valency of the ions, and, approximately, inversely

* *Ann. d. Phys.*, 83, 327 (1927).

† *Ibid.*, 85, 795 (1928).

proportional to the square root of the concentration. It may be expressed by the formula

$$A = 5.5 \nu_1^2 \nu_2^2 \sqrt{\frac{\sigma}{C}} 10^{-13},$$

where σ is the specific conductivity $\times \frac{1}{1000}$.

(c) A , besides being dependent on the valency and the conductivity, depends also to a certain extent on the nature of the ions.

(d) The second term B likewise increases with the product of the valencies, but much more slowly than A . In addition, it decreases with the concentration.

(e) With acetone as solvent the course of the phenomenon is the same, but A is greater, and B smaller, than for aqueous solutions under the same conditions.

Joos and Blumentritt* have extended Debye and Hückel's theory by considering the effect of high voltages. Their theoretical results indicate that the change in conductivity, δA , is given by

$$\delta A = AX^2 - BX^4 + CX^6 - \dots,$$

and with weaker fields by

$$\delta A = AX^2 - BX^4,$$

where, as before, A and B are constants. Blumentritt† found that, approximately, A was equal to $\frac{\nu^{3.5}}{\sqrt{D\eta}}$, where η is the viscosity of the solvent, and ν and D have their usual significance. In addition, B was equal to $\frac{D\nu}{\eta}$, approximately, for binary electrolytes containing similar ions.

These experimenters suggest three possible causes of the Wien effect: (a) a chemical effect due to the destruction of complexes by intense fields; (b) a decrease in the frictional resistance of the solvent, brought about by thermal effects and subsequent decrease in the viscosity of the solution—these two causes are quantitatively insufficient to account for the effect—and (c) a mutual braking, or slowing up, of the ions, arising from the presence of the ionic atmosphere.

If an ion is in motion under the action of an external electric field, there will be, as explained previously, an electrical charge density in the ionic atmosphere which is too small in front of, and too large behind, any ion upon which attention is fixed.

* *Phys. Zeits.*, 28, 836 (1927).

† *Ann. d. Phys.*, 85, 812 (1928).

Therefore, the ionic atmosphere will be asymmetrical, the asymmetry becoming more and more important, the greater the average ionic velocity. This asymmetrical electrical charge distribution will give rise to a resulting force called the *electrical force of relaxation*. When the force acting upon an ion is suddenly changed, it takes a finite time for equilibrium to be re-established. This time interval is known as the *time of relaxation*. Its value for various electrolytes, at a concentration of 0.001M and at 18° C., is given below. In addition, the wave-length corresponding to electrical oscillations, of periodic time equal to the times of relaxation, are included.

Electrolyte.	Time of Relaxation.	Corresponding Wave-length.
KCl	0.553×10^{-7} sec.	16.6 metres.
HCl	0.189×10^{-7} „	5.67 „
MgCl ₂	0.323×10^{-7} „	9.69 „
CdSO ₄	0.314×10^{-7} „	9.44 „
LaCl ₃	0.208×10^{-7} „	6.24 „

Although the degree of asymmetry can be calculated only approximately, even for small ionic velocities, the degree of accuracy obtained is usually sufficient.

When the applied electric fields are intense, the resulting values of the ionic velocities are high. In Wien's experiments, for example, they were of the order of one metre per second.

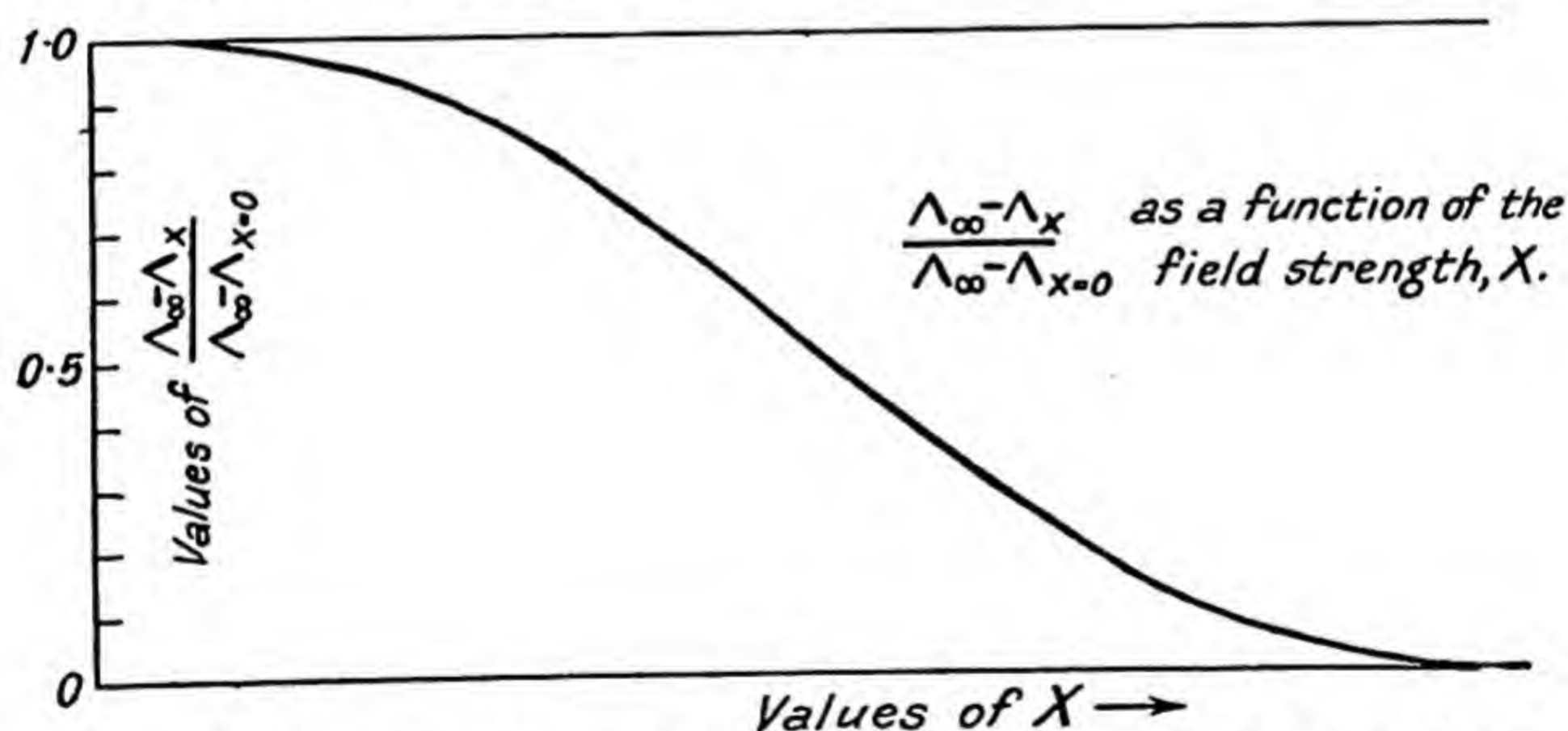


FIG. 57.—Variation of equivalent conductivity with applied electric force.

Under these conditions the ions will travel over a distance, many times greater than the thickness of the ionic atmosphere, during the time interval of relaxation. The ionic atmospheres can hardly be built up, and in such very strong fields the force of relaxation is of little, or no, consequence. Thus, the equivalent conductance under these conditions will approach the value found

at infinite dilution, and so at any given concentration the conductance increases as the electric intensity is raised. In Fig. 57 values of the electric force, X , are plotted, as abscissæ, against values of the function $\frac{\Lambda_0 - \Lambda_x}{\Lambda_0 - \Lambda_{x0}}$, as ordinates, where Λ_0 is the equivalent conductance at infinite dilution, Λ_{x0} , the value at any concentration, the electric field being very small, and Λ_x that at the same concentration, but with an electric field of strength X .

150. Conductance dispersion.—The conductance of an electrolytic solution also varies with the frequency of an applied alternating electric field. This effect is known as *conductance dispersion*. It may be measured by means of the arrangement shown in Fig. 58.

An oscillating circuit, A, contains a condenser, K, and a spark gap, F, whereby voltages up to 500,000 can be obtained and applied to the electrolyte, connected in at R_1 . A comparison

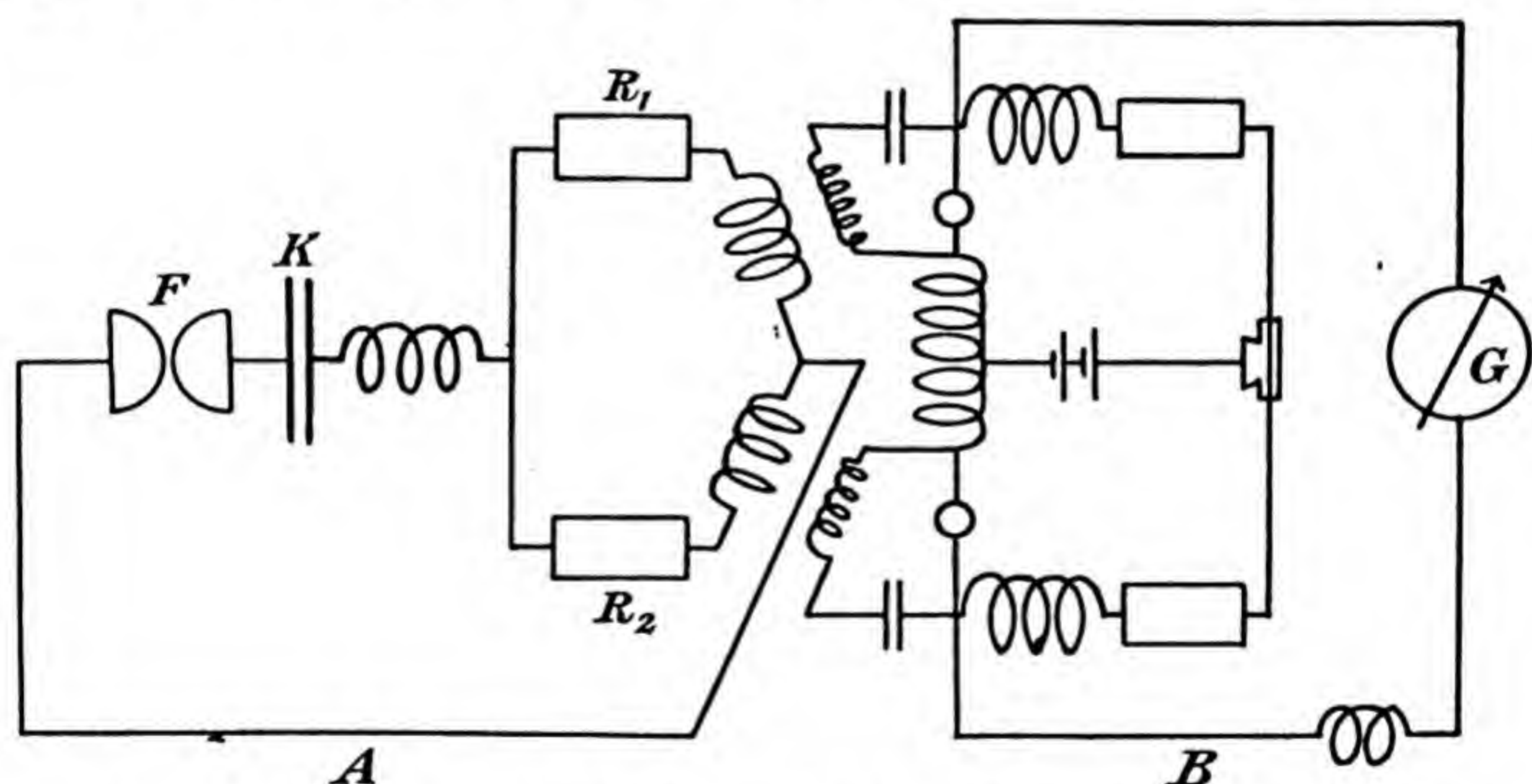


FIG. 58.—Measurement of the dispersion effect in electrolytic solutions.

liquid resistance is inserted at R_2 . If any difference occurs in the two resistances, a current is produced in the oscillating coupled circuit B, and actuates the galvanometer G.

If the frequency of the applied electric field is great enough, the electrical force of relaxation disappears, and since this force operates to resist the motion of an ion, it is evident that the conductance will increase if the frequencies are so high that the force does disappear. Thus, there is a variation in the electrolytic conductance with frequency.

Falkenhagen and Williams* expressed the molecular conductance, $\bar{\Lambda}$, as a function of the frequency of the electric field in the form

$$\bar{\Lambda} = \bar{\Lambda}_{\infty} - \bar{\Lambda}_1 - \bar{\Lambda}_2,$$

where $\bar{\Lambda}_{\infty}$ is the molecular conductance at infinite dilution, $\bar{\Lambda}_1$ the electrical force of relaxation, and $\bar{\Lambda}_2$, the ordinary force of electrophoresis,† both expressed as conductances. These experimenters found that the dispersion curve for magnesium chloride falls almost exactly along that for magnesium sulphate, and the curve for calcium ferricyanide lies between those for potassium ferricyanide and lanthanum chloride. The values of $\bar{\Lambda}_{\infty}$, $\bar{\Lambda}_1$ and $\bar{\Lambda}_2$ for different electrolytes are given below, C , the concentration, being expressed in moles per litre of solution.

Electrolyte.	Temperature.	$\bar{\Lambda}_{\infty}$.	$\bar{\Lambda}_1$.	$\bar{\Lambda}_2$.
KCl . . .	18° C.	130	$29.1 \times \sqrt{C}$.	$50.5 \times \sqrt{C}$.
HCl . . .	18° C.	380	$85.2 \times \text{"}$	$50.5 \times \text{"}$
LiCl . . .	18° C.	98	$22.0 \times \text{"}$	$50.5 \times \text{"}$
MgCl ₂ . . .	18° C.	222	$150 \times \text{"}$	$262.4 \times \text{"}$
MgSO ₄ . . .	18° C.	229	$410 \times \text{"}$	$404.0 \times \text{"}$
LaCl ₃ . . .	18° C.	345	$524 \times \text{"}$	$743.0 \times \text{"}$
K ₄ Fe(CN) ₆ . . .	25° C.	680	$1440 \times \text{"}$	$1890.0 \times \text{"}$
Ca ₂ Fe(CN) ₆ . . .	25° C.	620	$3920 \times \text{"}$	$2485.0 \times \text{"}$

The magnitude of the dispersion effect is recognised most simply when differences between the value of the molecular conductivity, for a definite frequency, and that for zero frequency are compared with the molecular conductance at infinite dilution, as in Fig. 59. Taking the example of K₄Fe(CN)₆, there is an increase in the molecular conductance of very dilute solutions of about 1 per cent. with wave-lengths corresponding to 16.3 metres. With diminishing wave-length the electrophoretic action remains unchanged but the relaxation effect decreases.‡

The various factors which influence the dispersion of electrical conductance have been investigated by Falkenhagen and Williams, and are summarised below, where $\omega\bar{\Lambda}_1$ and ${}_0\bar{\Lambda}_1$ are the relaxation effects at frequencies ω and zero, respectively.

(a) *Influence of concentration on dispersion.* The times of relaxation decrease with concentration, being inversely proportional to the concentrations.

(b) *Effect of mobility.* For any particular wave-length the values of $\frac{\omega\bar{\Lambda}_1}{{}_0\bar{\Lambda}_1}$ are much smaller for fast-moving ions than for the

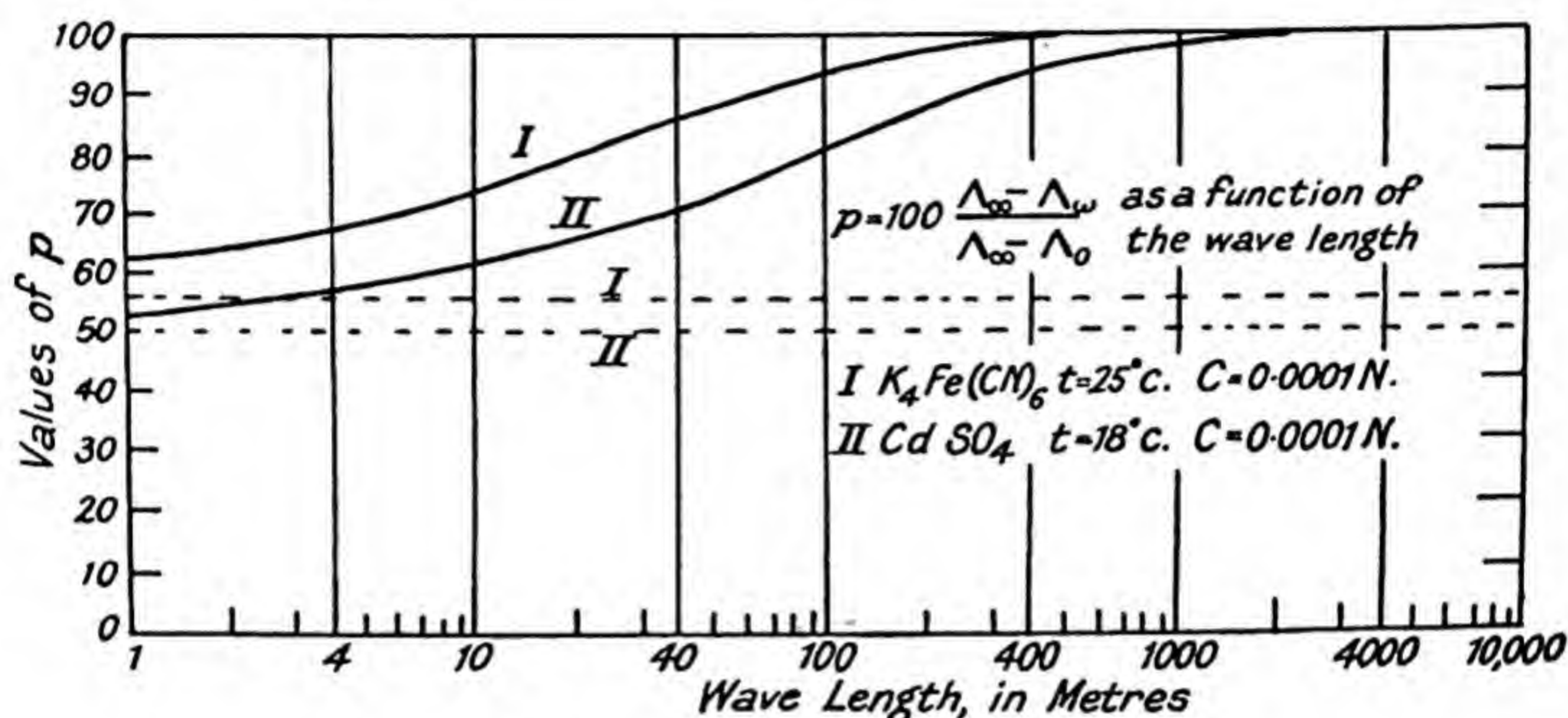
* *Jour. Phys. Chem.*, **33**, 1121 (1929).

† The viscous force exerted on the ions due to the action of the applied electric force on the ionic atmosphere.

‡ See Debye and Falkenhagen, *Phys. Zeits.*, **29**, 121 (1928).

slower ones. Thus, they are smaller for hydrochloric acid than for potassium chloride, and this is true for all wave-lengths.

(c) *Influence of dielectric constant.* For the same wave-length the value of $\frac{\omega\bar{\Lambda}_1}{\Lambda_0}$ decreases as the specific inductive capacity of the solvent decreases. In the case of methyl alcohol solutions a



Λ_∞ , Molecular conductivity at infinite dilution.
 Λ_ω , Molecular conductivity at frequency ω .
 Λ_0 , Molecular conductivity at zero frequency.

FIG. 59.—Variation of the molecular conductivity with wave-length.

smaller wave-length corresponds to the same value of $\frac{\omega\bar{\Lambda}_1}{\Lambda_0}$ for aqueous solutions.

(d) *Influence of temperature.* As the temperature rises the value of $\frac{\omega\bar{\Lambda}_1}{\Lambda_0}$ at any particular wave-length falls, and this is true for all wave-lengths. Hence at the higher temperatures appreciably smaller wave-lengths go with the same values of $\frac{\omega\bar{\Lambda}_1}{\Lambda_0}$.

151. Activity theory.—In recent years the attempt to interpret the properties of solutions of strong electrolytes in terms of the degree of dissociation, measured by the conductivity ratio, has been abandoned by some workers, and instead, much effort is being devoted to the exact determination of the thermodynamical properties of solutions. Lewis* introduced a term *fugacity* which is closely related to vapour pressure, and represents the tendency of a species to escape from solution. It is equal

* See Lewis and Randall, *Thermodynamics*.

to the vapour pressure if the vapour obeys the perfect gas laws, and we may, in fact, look upon it as an ideal vapour pressure, defining the ideal, or perfect, solution as one in which the fugacity of each constituent is proportional to the molar fraction * of that constituent. Thus, we may write for any component of a perfect solution,

$$f = f_0 N,$$

where f_0 , at a given temperature and pressure, is constant, N being the molar fraction of the component. It is advantageous to consider, at a given temperature, the ratio of the fugacity, f , of a substance in some given state to the fugacity, f_0 , in some state which, for temporary convenience, is chosen as a standard state. This *relative fugacity*, denoted by a , is termed the *activity*, and it is evident that in the standard state the activity, a_0 , is unity. For ideal solutions the activity is identical with the concentration, and is expressed as a molar fraction.

Since the fugacity, f , is similar to vapour pressure, and is actually equal to it, in value, if the vapour is an ideal gas, we may also define the fugacity in terms of the free energy at constant pressure, F , in the following manner,

$$F = RT \log f + B,$$

where B is a function of the temperature only. Hence, for an isothermal change in concentration the change in free energy, or the work obtainable, is given by

$$\delta F = RT \log \frac{f_2}{f_1},$$

or, since

$$a = \frac{f}{f_0},$$

$$\delta F = RT \log \frac{a_2}{a_1}. \quad . \quad . \quad . \quad (161)$$

Now the energy change, δF , expressed in electrical terms, is $\nu F E$, and thus the electromotive force of a cell without transference may be written in the form

$$E = \frac{RT}{\nu F} \log \frac{a_2}{a_1},$$

* The molar fraction is the ratio of the concentration of a component to the total concentration of all the solutes in a solution, the concentrations being expressed in moles per litre of solution.

whereas, assuming that the ions obey the laws of an ideal solute,

$$E = \frac{RT}{\nu F} \log \frac{\alpha_2 C_2}{\alpha_1 C_1}, \quad (162)$$

where C_1 and C_2 are the two concentrations and α_1 and α_2 , the degrees of dissociations at these concentrations. Now equation (162) will only hold at extremely high dilutions, when the variations of the solvent properties, with change in the concentration of the solute, tend to vanish. If the conditions are not so simple, corrections must be introduced into the above equation. Let us suppose that w_1 and w_2 are the energy corrections at concentrations C_1 and C_2 , respectively; then we may express the value of the electromotive force of the cell in the form

$$E = \frac{RT}{\nu F} \log \frac{C_2}{C_1} + w_2 - w_1,$$

or

$$E = \frac{RT}{\nu F} \log \frac{\gamma_2 C_2}{\gamma_1 C_1},$$

where γC may be considered as a corrected concentration and is equal to the activity a , γ being known as the *activity coefficient*. Thus we see that the measurement of the electromotive force of a cell gives the ratio of the ionic activities at two different concentrations. For example, if we consider a cell of the type



its electromotive force is given by equation (118), *i.e.*,

$$E = \frac{RT}{F} \log \frac{[\text{M}^+]_2 [\text{OH}^-]_2}{[\text{M}^+]_1 [\text{OH}^-]_1},$$

where the suffixes refer to the two concentrations.

Assuming that the activities of the kations and anions in any solution are the same,

$$E = \frac{RT}{F} \log \frac{(\gamma_2 C_2)^2}{(\gamma_1 C_1)^2} = \frac{2RT}{F} \log \frac{\gamma_2 C_2}{\gamma_1 C_1}.$$

From this result the ratio of two activities may be obtained, by extrapolation, for any two compositions that have not been directly investigated, and since at very great dilution, which Lewis estimates to be at 0.001 normal, $\gamma = 1$, we may write $\gamma_1 C_1 = C_1$. Thus the value of $\gamma_2 C_2$, the activity, and therefore the value of the activity coefficient, γ_2 , may be calculated. In this way we may determine the value of γ at different concentrations. These

values, for different electrolytes at different concentrations, have been calculated by Lewis and are given in Table LXVI.

TABLE LXVI.*

ACTIVITY COEFFICIENTS OF TYPICAL ELECTROLYTES IN AQUEOUS SOLUTIONS
AT 25° C.

Electrolyte.	Activity Coefficient at Molality							
	0.01M.	0.02M.	0.05M.	0.1M.	0.2M.	0.5M.	1M.	3M.
HCl924	.894	.860	.814	.783	.762	.823	1.35
LiCl922	.892	.843	.804	.774	.754	.776	1.20
NaCl922	.892	.842	.798	.752	.689	.650	.704
KCl922	.892	.840	.794	.749	.682	.634	—
KOH92	.89	.84	.80	.75	.73	.75	—
KNO ₃916	.878	.806	.732	—	—	—	—
AgNO ₃902	.857	.783	.723	.655	.526	.396	—
KIO ₃ , NaIO ₃882	.840	.765	.692	—	—	—	—
BaCl ₂716	.655	.568	.501	—	—	—	—
CdCl ₂532	.44	.30	.219	—	—	—	—
K ₂ SO ₄687	.614	.505	.421	—	—	—	—
H ₂ SO ₄617	.519	.397	.313	.244	.178	.150	.170
La(NO ₃) ₃571	.491	.391	.326	.271	—	—	—
MgSO ₄404	.321	.225	.166	.119	—	—	—
CdSO ₄404	.324	.220	.160	—	—	—	—
CuSO ₄404	.320	.216	.158	.110	.067	—	—

Now the value of the degree of dissociation, α , may be calculated from the formula

$$\alpha = \frac{\Lambda\eta}{\Lambda_0\eta_0},$$

and, utilising this expression, we can compare the corresponding values of α and γ at various concentrations, γ being determined from electromotive force measurements and α from the conductivity experiments. The results are shown in Table LXVII.

It will be observed that the activity coefficients decrease rapidly with concentration. In solutions of strong acids and bases the value of γ passes through a minimum, and then increases at higher concentrations. The higher the type of salt, the more rapidly does the coefficient decrease with increasing concentration. Whilst, as a rule, salts of the same type exhibit the same activity coefficients, a number of exceptions, such as those of cadmium chloride and barium chloride, occur.

Although the ionic concentrations in two solutions may be the same, the electric forces present in the liquids will be different

* See Lewis and Randall, *Thermodynamics*, p. 362.

TABLE LXVII.

COMPARISON OF ACTIVITY COEFFICIENTS WITH DEGREES OF DISSOCIATION
AT 25° C.

Moles of Electrolyte per 1000 Grams of Water.	NaCl.		KCl.	
	γ .	α .	γ .	α .
0.001	.977	.977	.977	.979
0.005	.946	.953	.946	.956
0.01	.922	.936	.922	.941
0.03	.869	.908	.869	.914
0.05	.842	.882	.841	.889
0.1	.798	.852	.796	.860
0.2	.752	.818	.749	.827
0.5	.689	.773	.682	.779
1.0	.650	.736	.634	.742

if the ions are of different valencies. To eliminate this difference in the electric forces Lewis and Randall introduced a quantity called the ionic strength, μ , which is obtained by multiplying the concentration of each ion by the square of its valency, and dividing the sum of the products by two. They were then able to state the general principle that, in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.

Activity mass law.—The mass law may be developed from the conception of activity in the following manner. Let us consider a solution in which a reaction takes place, such that p moles of the substance P, q moles of Q, etc., give r moles of R, etc., i.e.,



The free energy change at constant pressure in the reaction, when the substances are in any given state, is equal to

$$\delta F = (rF_R + sF_S + \dots) - (pF_P + qF_Q + \dots),$$

and if δF_0 is the free energy change when the components of the reaction are in the standard state,

$$\delta F_0 = (rF_{R_0} + sF_{S_0} + \dots) - (pF_{P_0} + qF_{Q_0} + \dots).$$

If a_P , a_Q , etc., represent the activities of the components in the given state, then from equation (161),

$$p(F_P - F_{P_0}) = RT \log a_P^p, \text{ etc.},$$

and thus,
$$\delta F - \delta F_0 = RT \log \frac{a_R^r a_S^s \dots}{a_P^p a_Q^q \dots}.$$

For equilibrium, $\delta F = 0$,

and therefore,
$$\delta F_0 = -RT \log \frac{a_R^r a_S^s \dots}{a_P^p a_Q^q \dots}$$

For a constant temperature,

$$\delta F_0 = -RT \log K,$$

where K is the equilibrium constant under constant pressure conditions.

If the solution is ideal,

$$\frac{a_R^r a_S^s}{a_P^p a_Q^q} = \frac{C_R^r C_S^s}{C_P^p C_Q^q} = K,$$

and supposing that $\frac{\Lambda}{\Lambda_0}$ gives the degree of dissociation at each concentration, we have, in the case of a binary electrolyte, assuming that the activity of each component is equal to its concentration,

$$\frac{\frac{C\Lambda^2}{\Lambda_0^2}}{\left(1 - \frac{\Lambda}{\Lambda_0}\right)} = K.$$

Thus K is not a constant unless the various assumptions quoted above are correct. In general, however, we can assume that as infinite dilution is approached, K represents the true equilibrium constant.

Activity from freezing-points.—We have seen in section (65) that the van't Hoff factor, i , may be used to interpret dilute electrolytic solutions by considering $(i - 1)$ as a measure of the degree of dissociation of binary electrolytes, but it does not give the thermodynamical degree of dissociation.

Lewis and Linhart* found that electrolytes of all the various types investigated approach, as a limiting law in dilute solutions, the relationship expressed by

$$1 - \frac{\delta T}{nC\tau} = \beta C^b,$$

where n is the number of ions which each molecule produces when completely dissociated, δT , the observed lowering of the freezing-point temperature, produced by a salt at a concentration of C moles of solute per 1000 grams of water, τ , the theoretical molecular depression, and β and b , constants. By combining

* *Jour. Amer. Chem. Soc.*, 41, 1951 (1919).

this empirical expression with the thermodynamical equation connecting free energy of dilution with the lowering of the freezing-point, Lewis and Linhart obtained the equation,

$$\log \gamma = - \frac{\beta(b+1)C^b}{b}, \quad (163)$$

and by employing this equation, they obtained a series of values of γ for various electrolytes.

If we compare these values with the values of $\frac{\Lambda}{\Lambda_0}$, which are ordinarily used as a measure of the degree of dissociation, there is a great divergence between them, this divergence increasing with salts of the higher types. In addition, since the heat of dilution is negligible, the values of γ must be independent of the temperature. On the other hand, the values of $\frac{\Lambda}{\Lambda_0}$ decrease markedly with temperature.

Activity coefficients of individual ions.—If we have a solution such as sodium chloride, we may denote the activities of the kation and anion by a_+ and a_- , respectively, while a represents the activity of the undissociated sodium chloride molecule. In this case the thermodynamic equation of equilibrium takes the form

$$\frac{a_+ a_-}{a} = K.$$

At infinite dilution we consider the activity of each ion of sodium chloride to be equal to its concentration, so that if we choose some standard state, such that $K = 1$, we can define the activity of sodium chloride as the product of the activities of its two ions, viz.,

$$a_+ a_- = a.$$

At infinite dilution $a_+ = a_- = a^{\frac{1}{2}}$, and if we denote the geometrical mean of the two ion activities by a_{\pm} , then,

$$a_{\pm} = (a_+ a_-)^{\frac{1}{2}} = a^{\frac{1}{2}},$$

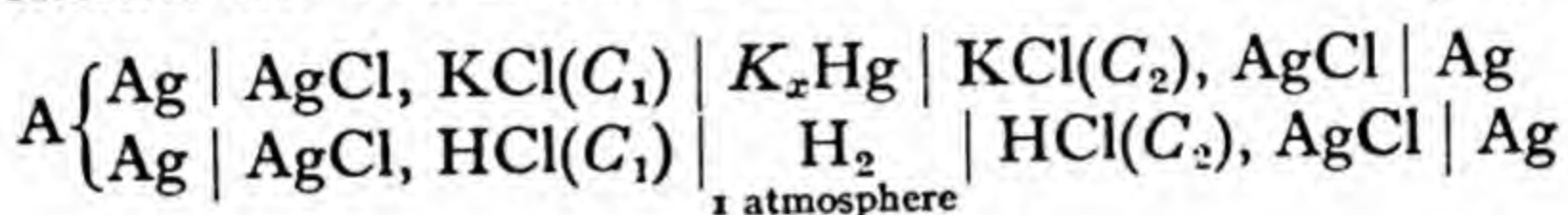
a_{\pm} being called the *mean activity*.

At infinite dilution the activity coefficient is the same for all ions, and equal to unity, and as the concentration increases, we should expect that the activity coefficients of two ions of similar type would remain approximately the same, up to moderately concentrated solutions.

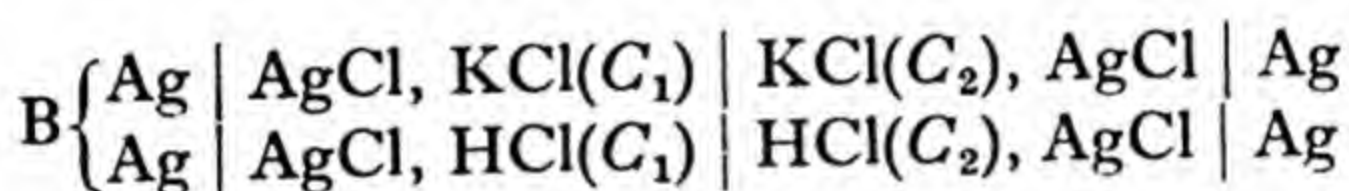
It is evident that if we ascertain, or arbitrarily assume, the

individual activity coefficient of some one ion at a given ionic strength, we can then proceed to determine the values for other ions, since in dilute solutions the activity coefficient of any ion depends solely upon the total ionic strength of the solution. Thus, with a given value of μ , the ionic strength, if we knew the activity coefficient of the sodium ion, we could combine this with the known activity coefficient of sodium chloride to obtain the value for the chloride ion. Using, then, the known value for barium chloride we could obtain that for the barium ion. MacInnes* has suggested that at each concentration the two ions of potassium chloride should be considered to possess equal activity coefficients. If this is the case, then a table of individual activity coefficients for all ions may be obtained. He determined the activity of the hydrogen ion in the following way:—

Consider the two sets of cells, without and with transport,



and



Then,

$$E_A = \frac{RT}{F} \log \frac{a_1^+ a_1^-}{a_2^+ a_2^-},$$

and

$$E_B = \frac{n_K RT}{F} \log \frac{a_1^+ a_1^-}{a_2^+ a_2^-},$$

where n_K is the transference number for the kation.

For the potassium chloride solutions we assume that $a_1^+ = a_1^-$, and $a_2^+ = a_2^-$, and find the value of the ratio $\frac{a_1^-}{a_2^-}$ for the chloride ion at the concentrations C_1 and C_2 . From the electromotive force data for the hydrochloric acid cell, at the same concentrations, we can find, by subtracting the above value of $\frac{a_1^-}{a_2^-}$ in the

appropriate equation, the value of $\frac{a_1^+}{a_2^+}$ for the hydrogen ion.

At very great dilution we assume that the activity is equal to the degree of dissociation, *i.e.*, $\alpha = \gamma$, and since α is the same for potassium chloride as for hydrochloric acid, it follows that the value attributed to γ for potassium chloride, at great dilution, is the same as the value to be attributed to hydrochloric acid, likewise

* *Jour. Amer. Chem. Soc.*, 41, 1086 (1919).

at great dilution. With this as the starting-point, and knowing the value of $\frac{a_1^+}{a_2^+}$ for the hydrogen ion at other dilutions, from electromotive force measurements, we can calculate the absolute values of the hydrogen ion activity in hydrochloric acid at any concentration.

BIBLIOGRAPHY.

- Blumentritt, *Ann. d. Phys.*, **1**, 195 (1929).
 Bjerrum, *Det. Kgl. Danske Viden. Sels.*, **7**, 9 (1926).
 Bjerrum and Larsson, *Zeits. phys. Chem.*, **127**, 358 (1927).
 Bray, *Jour. Amer. Chem. Soc.*, **49**, 2372 (1927).
 Brodsky, *Zeits. phys. Chem.*, **121**, 1 (1926).
 Bronsted and Williams, *Jour. Amer. Chem. Soc.*, **50**, 1338 (1928).
 Debye, *Trans. Amer. Electrochem. Soc.*, **51**, 507 (1927).
 Ebert, *Zeits. phys. Chem.*, **122**, 28 (1926).
 Evjen and Zwicky, *Phys. Rev.*, **33**, 860 (1929).
 Falkenhagen, *Phys. Zeits.*, **30**, 163 (1929).
 Fredenhagen, *Zeits. phys. Chem.*, **128**, 1, 239 (1927); **140**, 65, 435 (1929).
 Frenkel and Finkelstein, *Zeits. f. Phys.*, **35**, 239 (1925).
 Gronwall, la Mer and Sandved, *Phys. Zeits.*, **29**, 358 (1928).
 Gross and Halpern, *ibid.*, **26**, 636 (1925).
 Gyemant, *ibid.*, **29**, 289 (1928).
 Harned, *Jour. Amer. Chem. Soc.*, **48**, 326 (1926); *Jour. Phys. Chem.*, **30**, 433 (1926).
 Harned and Åkerlöf, *Phys. Zeits.*, **27**, 411 (1926).
 Harned and Fleysher, *Jour. Amer. Chem. Soc.*, **47**, 82 (1925).
 Hückel, *Phys. Zeits.*, **26**, 93 (1925); *Zeits. Elektrochem.*, **34**, 546 (1928).
 La Mer, *Trans. Amer. Electrochem. Soc.*, **51**, 507 (1927).
 Lowry, *Phil. Mag.*, **6**, 50 (1928).
 Lucasse, *Jour. Amer. Chem. Soc.*, **48**, 626 (1926).
 MacInnes, *ibid.*, **48**, 2068 (1926).
 Müller, *Phys. Zeits.*, **28**, 778 (1927).
 Nernst, *Zeits. Elektrochem.*, **33**, 428 (1927); *Preuss. Akad. Wiss. Berlin, Ber.*, **1**, 4 (1928).
 Nonhebel and Hartley, *Phil. Mag.*, **2**, 586 (1926); **50**, 729 (1925).
 Noyes and Baxter, *Jour. Amer. Chem. Soc.*, **47**, 2122 (1925).
 Onsager, *Jour. Phys. Chem.*, **32**, 1461 (1928).
 Pike and Nonhebel, *Phil. Mag.*, **50**, 723 (1925).
 Scatchard, *Phil. Mag.*, **2**, 577 (1926).
 Schiller, *Ann. d. Phys.*, **83**, 137 (1927).
 Schreiner and Frivold, *Zeits. phys. Chem.*, **124**, 1 (1926).
 Sherrill and Noyes, *Jour. Amer. Chem. Soc.*, **48**, 1861 (1926).
Trans. Farad. Soc., **24**, 334 (1927); **15**, 3 (1919).
 Tretjakov, *Zeits. Elektrochem.*, **35**, 440 (1929).
 Wien, *Ann. d. Phys.*, **1**, 400 (1929).
 Wilke, *Zeits. phys. Chem.*, **121**, 401 (1926).

CHAPTER XI.

TECHNICAL APPLICATION OF ELECTROLYSIS.

152. Electrolytic deposition.—The principles of electrolysis are applied in many technical processes, and although we are mainly concerned with the actual principles, some of the processes will be considered. One such application is *electro-refining*, in which soluble anodes of the metal to be refined are immersed in a bath containing a salt of the metal, the kathode usually consisting of thin sheets of the pure metal. Theoretically, the pure metal is deposited upon the kathode, an equivalent amount being dissolved from the anode; the impurities either remain undissolved in the solution, or, if dissolved, they are not deposited upon the kathode.

In *electro-plating* a thin smooth coherent film of metal is deposited upon an article, acting as the kathode in an electrolytic bath, the concentration of the solution being maintained constant by using, as anodes, metal similar to that which is to be deposited. The film must be capable of taking a high polish.

Electrolysis will occur in a bath when the externally applied potential difference is equal to the sum of the various potential differences, which exist within the bath. These include the electrode potentials, overvoltages at the electrodes and the potential drop through the electrolytic solution. The decomposition voltage depends upon many factors, such as the state and nature of the electrodes, concentration of the electrolyte and temperature, and before deposition of ions upon a kathode can take place the potential difference, applied across the solution-electrode interface, must be a little greater, in value, than the sum of the electrode potential, π , and the overvoltage, π_{ov} , at the electrode. Thus, if π_D represents this deposition potential difference,

$$\pi_D = \pi + \pi_{ov},$$

where

$$\pi = \pi_0 + \frac{RT}{\nu F} \log [C] \quad . \quad . \quad . \quad (164)$$

π_0 being the normal electrode potential and $[C]$ the ionic concentration.

Let us consider the case of a copper electrode immersed in an acid solution containing a normal concentration of copper ions. Since the normal electrode potential of this metal is $+0.347$ volt, the application of a potential difference of -0.347 volt, measured from the liquid to the metal, will just balance the electrode potential in the absence of any type of overvoltage, and a slightly greater value will cause deposition. But, as shown above, the electrode potential depends upon the concentration of the copper ions within the solution, and as this concentration decreases, the potential difference, required to deposit a further amount of copper, increases, so that finally, if the process is allowed to continue and the copper ions within the solution are not replenished, the applied potential difference becomes great enough to deposit hydrogen ions.

It is evident that those ions possessing the lowest value of the deposition potential will be deposited first from a solution containing a mixture of ions. For example, suppose that the solution consists of 0.1 normal lead nitrate and 0.1 normal nickel nitrate, and contains a lead kathode with a platinum anode. The normal electrode potential of $\text{Pb} | \text{Pb}^{++}$ is -0.129 volt and that of nickel -0.22 volt, at 18°C. , both referred to the normal hydrogen scale, so that the electrode potentials in the solution are -0.158 volt and -0.249 volt, respectively, if we assume that the lead kathode behaves towards the nickel salt, as regards the electrode potential, in a manner similar to that of a nickel electrode. Thus, since the kathode $| \text{Pb}^{++}$ junction has a greater positive potential than the kathode $| \text{Ni}^{++}$ junction, lead alone will be deposited from solution until the concentration of the lead ions in the solution has fallen so low that the potential of the kathode $| \text{Pb}^{++}$ interface reaches the value -0.249 volt, *i.e.*, it must decrease by 0.091 volt. But a ten-fold concentration change varies the electrode potential, at 18°C. , by 0.029 volt, equation (111), so that the decrease, 0.091 volt, is produced by a concentration change of the lead ions from 0.1 to 0.0001 normal. At this stage both metals will be deposited simultaneously. It will be noted that overvoltage has not been taken into account.

It is also possible to deposit both metals together by using such a large current that the actual layer of the solution in contact with the kathode is exhausted of lead ions, the nickel metal then being deposited by the current. Thus one can form alloys of different composition by varying the conditions as regards current, temperature or ionic concentration.

153. Current efficiency.—Hydrogen plays an important part in electrolytic separation. In some cases hydrogen may be de-

posited instead of the metal ; for example, as shown in the previous section, if we have an acid solution of copper sulphate containing a normal concentration, both of the copper and the hydrogen ions, the potential of the copper kathode would be $+ 0.347$ volt, and that of the hydrogen electrode zero. As the concentration of the hydrogen ions is raised and that of the copper ions decreased, the hydrogen potential of the kathode increases while the copper potential decreases, and if the changes in concentration are carried far enough, the copper potential falls below that of the hydrogen. In these circumstances hydrogen and not copper will be deposited. The current which passes under these conditions is used for the evolution of hydrogen, and not for the production of metallic copper, so that the process is inefficient. We may define the current efficiency, or rather the kathode efficiency, as the ratio of the weight of the metal actually deposited to that which would be deposited if none of the current were utilised in evolving hydrogen.

When we pass on to consider the deposition of a metal which has a lower electrode potential than that of the hydrogen electrode, it is evident that hydrogen will be deposited instead of the metal, unless the cathodic overvoltage at the metal is high. Thus, in depositing nickel from a strongly acid nickel salt solution, since the cathodic overvoltage is, approximately, $- 0.21$ volt and the normal electrode potential of nickel $- 0.22$ volt, the process is a very inefficient one, most of the current being used to produce hydrogen, and this inefficiency will become more pronounced as the solution is made more and more dilute. If the nickel salt solution is neutral, or nearly so, the hydrogen evolution is minimised because the equilibrium potential of the electrode $H_2 | \text{neutral solution}$, referred to the normal hydrogen scale, is $- 0.406$ volt, approximately, and owing to the cathodic overvoltage, hydrogen is not likely to be evolved until the applied potential difference, measured from the solution to the kathode, attains a value greater than $+ 0.62$ volt, which is greater than that required to deposit nickel.

There is, however, in this case a further difficulty. The discharge of any hydrogen from a solution depletes the latter of the hydrogen ions and, consequently, there remains within the vicinity of the kathode an excess of hydroxyl ions, so that the hydroxide of the metal is liable to be deposited. This deposit prevents the attainment of the requisite potential for the metal deposition and, in addition, the hydroxide deposit will be intermingled with the metal, producing a kind of spongy deposit. It is evident, therefore, that the hydrogen ion concentration in the solution must be maintained as low as possible, without thereby allowing deposits which

are contaminated with these hydroxide, or basic, precipitates. The latter can be avoided by including in the electrolytic solution certain substances, called *buffering agents*, which maintain the hydrogen ion concentration above that required for the hydroxide precipitation, however much hydrogen is discharged at the kathode. These buffering agents react with the hydroxyl ions, liberated within the neighbourhood of the kathode and in so doing leave the hydrogen ion concentration constant. Hence we see that the pH value of the solution is extremely important. This value is affected by temperature changes. Until recently, the effect of the temperature of the solution on the pH value was neglected. For instance, if a standard nickel solution has, what is considered good practice, a pH value of 5.8 at $70^{\circ} F.$, this value becomes 6.2 at $40^{\circ} F.$, and 5.4 at $130^{\circ} F.$

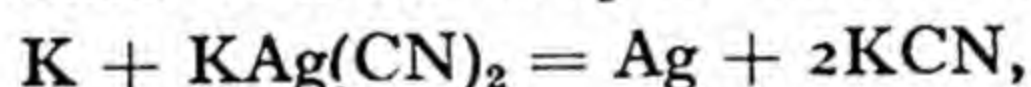
Since a dilute solution is favourable to the formation of the hydroxide, in order to deposit metals of lower electrode potential than that of the normal hydrogen electrode, it is necessary to employ concentrated metallic salt solutions in which the kathode potential, at which deposition occurs, is as slightly negative as possible. In addition, the hydrogen ion concentration must be kept as low as possible, consistent with no hydroxide precipitation, *i.e.*, the hydrogen potential must be as negative as possible. Another interesting fact in connection with nickel deposition is that although its electrode potential for a normal salt solution is more positive than that of hydrogen at a pH value of 5.8, yet the deposition of nickel is always accompanied by hydrogen evolution, even at small current densities. Smits* found that the electrode potential of nickel in a normal nickel sulphate solution was -0.194 volt, when the metal had been freed from hydrogen, but that it decreased with time to -0.35 volt. From this fact he suggests that the hydrogen evolution can be explained by the formation of an alloy between the gas and the nickel.

As the electrode potential of a metal decreases, deposition of the metal becomes increasingly more difficult, although zinc is an exception. With this metal the hydrogen overvoltage is so great that it effectively prevents the liberation of hydrogen from acid solutions of zinc salts, despite the fact that the electrode potential of this metal is -0.76 volt. The high cathodic overvoltage value only applies to a smooth zinc surface, and if the surface becomes rough, or spongy, the overvoltage falls, and hydrogen is liberated. The gas is also evolved if the current density is very high. In this case the zinc ionic concentration, in the immediate neighbourhood of the kathode, is decreased, so that the zinc electrode potential is lowered.

* *The Theory of Allotropy*, 1922.

Many metals cannot be deposited at all from aqueous solutions of their salts, but in these cases it is probably impossible to obtain a solution containing anything like a normal concentration of the metal ions, and therefore the electrode potential is greatly depressed below that of the normal hydrogen electrode.

When we are dealing with complex salts in solution the metallic ion concentration is very low, and even for low current densities the polarisation is considerable. This is due to the comparative paucity of the metallic ions in the bath solution, local exhaustion of ions readily occurring. Complete exhaustion at the kathode surface never occurs, since the metallic ions are replaced by dissociation of the complex anions. Complex salts in plating processes have been long employed in practice, as they give smooth deposits—so fine as to be apparently structureless. These fine deposits are obtained if the deposition is fairly rapid, although it must not be too rapid, otherwise a spongy mass is liable to be formed. A slow deposit gives, in general, a rough surface. Dean and Cheng* have offered another explanation of this action with complex salts. They suggest that in the electrolysis of the complex salt, $\text{KAg}(\text{CN})_2$, for example, the potassium ions, K^+ , are discharged and form an alloy with the kathode metal. The potassium then reacts with the complex salt thus :



and thus the metallic silver is produced by a secondary reaction.

154. Alloys.—If two metals are deposited practically reversibly, their simultaneous deposition is, in general, only possible when the values of their electrode potentials are nearly equal. Although the normal electrode potentials of two metals may differ widely, the considerable polarisation effects, that occur when metals are deposited from solutions in which they exist in the form of complex anions, may equalise the values of the deposition potential of the two metals. For example, Spitzer† has shown that these values for copper and zinc, at different current densities and in different solutions, are as follows :—

Current Density (amps./cm. ²).	Deposition Potential (Volts).			
	$\text{CuSO}_4(\text{N})$.	$\text{KCuCy}_2(0.1\text{N})$.	$\text{ZnSO}_4(\text{N})$.	$\text{K}_2\text{ZnCy}_2(0.1\text{N})$.
0.000	+ 0.302	− 0.610	− 0.795	− 1.033
0.001	+ 0.273	− 0.77	− 0.829	− 1.12
0.003	+ 0.262	− 1.12	− 0.838	− 1.25

* *Met. Chem. Eng.*, 19, 83 (1918).

† *Zeits. Elektrochem.*, 11, 345 (1905).

so that although it is hopeless to expect that zinc will be deposited from a $\text{ZnSO}_4\text{-CuSO}_4$ solution while any copper remains, a cyanide bath containing both metals may be used to effect simultaneous deposition, provided that a suitable current density is employed, and thus a layer of brass is obtained upon the kathode.

In other cases simultaneous deposition of metals of different electrode potential occurs if the baser metal alloys with the nobler metal, the deposition potential of the alloy being less negative than that of the more reactive constituent. Magnesium cannot be prepared from aqueous solutions, but iron-magnesium alloys have been obtained by electrolysis of a solution containing magnesium chloride and iron sulphate. In a similar manner a nickel-magnesium alloy can be formed from a bath containing normal NiSO_4 and normal MgSO_4 .

Two metals are not always deposited in the proportions expected. Thus, Schoch and Hirsch* have shown that a bath containing zinc and nickel sulphates, of equal concentrations, gives an alloy containing much more zinc than nickel, although from their electrode potentials one would expect the nickel to predominate.

The simultaneous deposition of copper and zinc from their sulphate solutions only occurs if the current density is high, and if there is a much greater concentration of zinc ions than of copper ions in the solution. Under these conditions the solution near the kathode becomes deficient in copper ions, so that the potential rises until the zinc deposition potential is attained.

155. The Electrolysis bath.—In practice the potential drop across the electrodes in an electrolysis bath seldom exceeds 6 volts, and, as a rule, a number of these baths are placed in series. The current may range from 1,000 to 10,000 amperes, and the arrangement of the electrodes in the bath varies considerably. In metal refining, a large number of anodes are arranged in parallel and a common bus bar used, the anodes alternating with a similar set of kathodes. In other arrangements the electrodes are fixed in the bath parallel to one another, in such a way that they act as bipolar electrodes, one side being the anode and the other the kathode, the two end electrodes being connected to the external source of electromotive force. These different arrangements are illustrated in Fig. 60.

The important features of the electrodes are (a) their chemical resistivity, and (b) their overvoltage for the gas, or gases, which

* *J. Amer. Chem. Soc.*, 29, 314 (1907).

are liable to be liberated at their surfaces. The most important cathodic materials are iron, platinum, lead, mercury and graphite. Iron is generally used with alkaline solutions, graphite as the kathode in acid solution, and mercury as the kathode in a certain class of alkali-chlorine cell. In the latter case, the object is to produce a sodium, or potassium, amalgam without the simultaneous evolution of hydrogen, and the fact that hydrogen overvoltage at mercury is high makes this possible.

The anode material is of great importance in view of its general liability to attack by anodic chlorine or oxygen. Graphite anodes

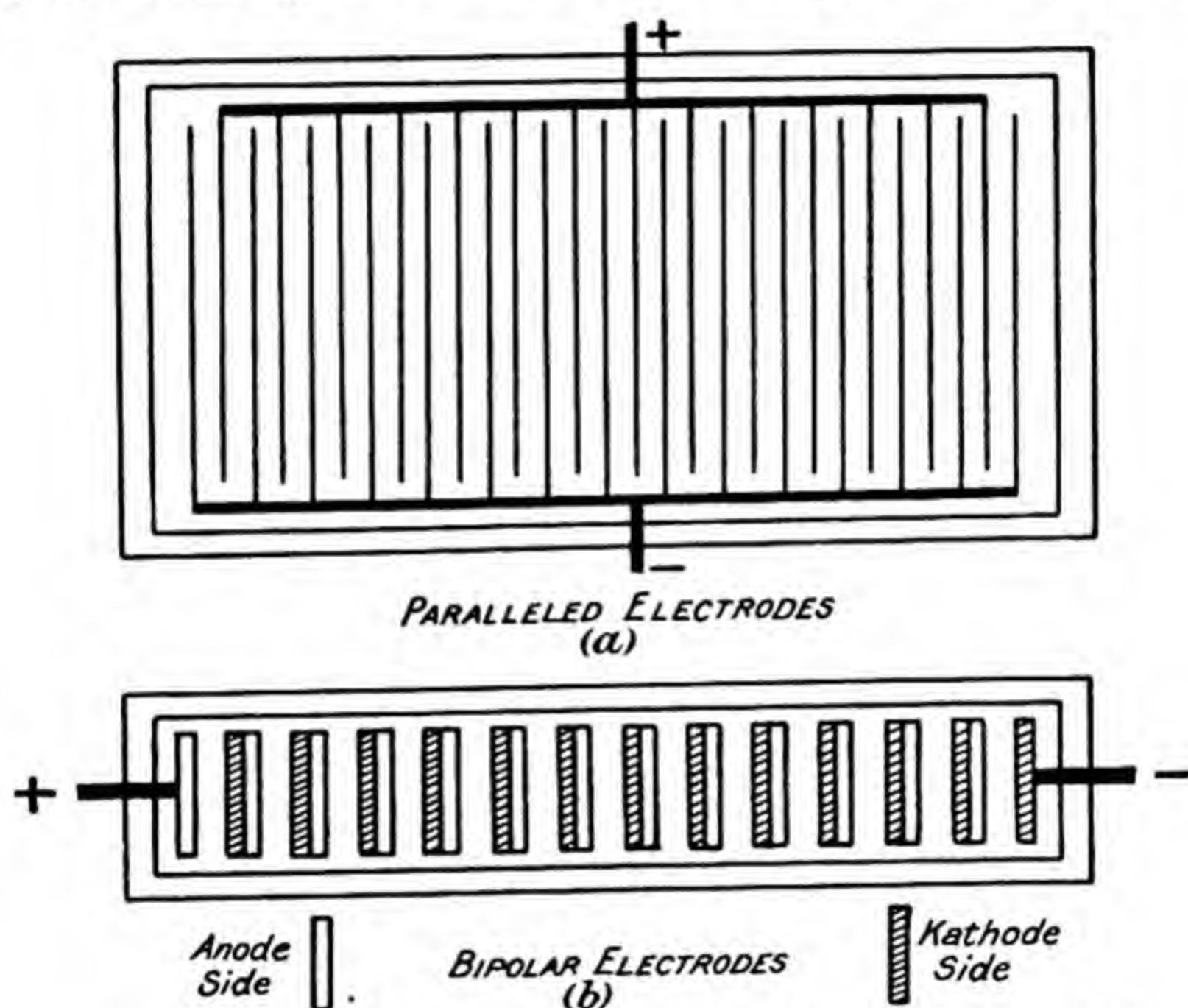


FIG. 60.—Arrangement of electrodes in the electrolysis bath.

have almost completely replaced hard carbon anodes in brine electrolysis. Both types are very resistive to chlorine, but the varying quantities of oxygen, which are invariably produced anodically in brine cells, attack the hard carbon far more readily than graphite. For use with alkaline electrolytes evolving oxygen, iron, or nickel, can be employed. In acid solutions iron can sometimes be used, but platinum is, from a chemical point of view, more satisfactory.

156. Electro-plating.—From what has been said previously, a solution from which the metal is to be electro-deposited must contain a representative from one, or more, of the following classes

of substances : (a) a salt containing the metal to be deposited, (b) conducting salts, (c) addition agents.

The salt of the metal, used as constituent of a plating solution, is usually either the sulphate, or the double cyanide. Sometimes, though less frequently, some other salt is used, such as zinc chloride in some zinc baths and lead acetate in lead baths. The sulphate is much to be preferred, for one knows with greater certainty what takes place at the electrodes during electrolysis of a bath containing it, and so there is greater control over the working conditions.

The conducting salts are usually salts of ammonia, such as the sulphate or the chloride. At times, the sulphate, or the chloride, of a metal of the alkali, or of the alkaline earth group, is employed. Thus sodium sulphate in an iron bath, and sodium chloride in a nickel bath are used. The function of the conducting salt is to decrease the electrical resistance, so that the required electromotive force is less, and the kathode potential fall correspondingly lowered. Hydrogen is then less likely to be liberated. The use of these conducting salts also possesses other advantages, as may be shown in the following manner. If a nickel bath is used and contains the sulphate only, no useful deposit is obtained, but if sulphate of ammonia, or nickel ammonium sulphate is added, then the nickel deposit is satisfactory. The added ammonium sulphate forms a complex salt with the nickel sulphate, and this complex salt ionises into NH_4^+ and $\text{Ni}(\text{SO}_4)_2^-$. The kation is discharged at the kathode and reacts with the double salt in the neighbourhood, replacing nickel and giving rise to ammonium sulphate. The hydrogen is thus formed as the result of a secondary reaction and not from the discharge of hydrogen ions upon the kathode. Hence, in addition to lowering the kathode fall, the conducting salt causes the nickel to be deposited as the result of a secondary and purely chemical reaction, instead of directly and immediately after discharge of the nickel ions.

The addition agents, when present in solution, frequently enable a deposit to be obtained when otherwise a poor deposit, if any, would result. A case in point is lead. No solution is known from which this metal can be deposited in coherent and small grain form in the absence of some addition agent, such as peptone, or olive oil. In the case of zinc also, all the best baths used contain a small amount of some addition agent, such as gelatine or dextrin. An addition agent, which produces a good result in any particular case, may be found to have injurious effects upon the structure of the deposit of another metal.

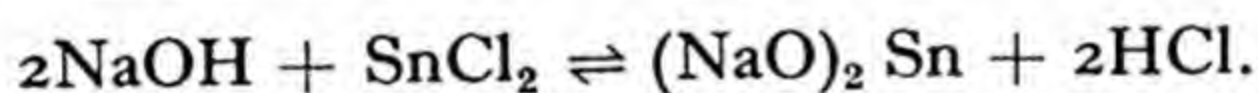
The conducting salt employed should contain, if possible, the same acid radical as does the salt of the metal to be deposited.

Ammonium sulphate and not the chloride is used generally, in nickel sulphate baths, and, as a result, the number of different types of anions discharged at the anode is lessened. Consequently what is happening at the anode is known fairly well, and a better control can be maintained over the general working of the bath.

In all good solutions the anode and kathode efficiencies will be nearly 100 per cent. Usually, the anode efficiency is lower than that at the kathode, which means that metal is taken out of the solution faster than it is supplied to it. Thus the bath will gradually become poor in metal contents, and metal must be supplied from outside, *i.e.*, by the addition of metal salts, but this practice is not to be encouraged. The electro-plating by some metals will now be considered.

Tin.—The type of solution for tin-plating baths which has been most widely used is one proposed by Elsner * It is based upon the protochloride of tin dissolved in caustic soda or caustic potash. If a really thick deposit is required, a colloid must be added to the bath, and it is advisable to use a bath of the acid type—one, for instance, containing oxalates and oxalic acid, or phosphates and phosphoric acid.

In the alkaline bath the following reaction occurs :



The composition of the solution will soon become complicated by reason of the alteration of the substances present. No alkaline bath can be stable, or immune from chemical alterations, and the reactions that result in deposition are not known with any degree of accuracy.

The current density should be as great as possible, and the E.M.F. should be 3-4 volts at a distance of 9-10 ins. between the electrodes. Anodes of good cast metal only should be used.

The only acid bath that has been shown to be at all satisfactory is that devised by Mathers.† The composition is 5 per cent. of stannous oxalate, 6 per cent. of ammonium oxalate, $1\frac{1}{2}$ per cent. of oxalic acid, and $1\frac{1}{4}$ per cent. of peptone. The current density should be 4 amperes per square foot, and the temperature, ordinary. Any lack of metal in the bath is shown by the deposit becoming dark, and an addition of stannous oxalate must then be made. During electrolysis, a fine yellow precipitate forms in the bath and settles to the bottom as long as sufficient oxalic acid is present. This is probably a complex salt of tin, and so even when

* See Langbein, *Electro-deposition of Metals*, 440 (1909).

† *Trans. Amer. Electrochem. Soc.*, 29, 411 (1916).

the bath functions well, metal is precipitated from the solution as a constituent of a salt, and is therefore lost to that extent. The only way to replenish the metal is to add stannous oxalate. In spite of these additions, the bath finally becomes so deteriorated that bright solid deposits can no longer be obtained.

Lead.—Three lead-plating baths are available ; they all contain an organic addition agent and free acid. Mathers' * perchlorate bath contains 4.5 per cent. of perchloric acid, 5.4 per cent. of lead perchlorate, and 0.05 per cent. of peptone. Later † he found that lead acetate could replace the perchlorate, and ammonium, or sodium perchlorate, and glue can be used in place of the acid and peptone. The anode and kathode efficiencies are nearly 100 per cent., and there is only a slight loss of perchloric acid by reduction. The current density should be 18 to 20 amperes per square foot, the bath should be worked at 60° to 70° F., and the anodes should be of good sheet-lead.

Betts and Kern ‡ used a bath containing 13.5 per cent. of lead fluosilicate, 6.5 per cent. of hydrofluosilicic acid, and about 1 gram of gelatine to 2,000 cubic centimetres of solution. The temperature was ordinary, and the current density, 10 to 20 amperes per square foot.

Zinc.—Zinc sulphate is undoubtedly the best metal-containing salt to use in this case, and among the many conducting salts which have been used are sodium sulphate, sodium chloride, magnesium sulphate, aluminium sulphate and zinc chloride. Boracic acid is a good addition agent, and aluminium sulphate cuts down the size of the grains of the deposit. Glue and sugar have also been used as addition agents.

A good bath solution is one containing 3 lbs. of zinc sulphate per gallon of water, 2 ozs. of common salt, 3 ozs. of boracic acid, aluminium sulphate 3 to 4 ozs., and a little sugar, maltose or dextrin. The quantity of sugar used is variable, but 1 to 3 ozs. will usually be sufficient. The principal reactions are, the liberation and solution of zinc, the prevention of the formation of the oxides and hydroxides by the boracic acid, and diminution of the size of the grains of the deposit by the aluminium sulphate.

The current density is 10 amperes per square foot, the E.M.F. is usually 2 to 2.5 volts at a distance of 9 ins., and the temperature is ordinary. Agitation of the kathode is useful, but not absolutely necessary. The anodes should be of good rolled zinc, as pure as can be obtained commercially, and in size and number they should be as large, and as many, as the vat will accommodate.

* *Trans. Amer. Electrochem. Soc.*, 17, 261 (1910).

† *Ibid.*, 24, 315 (1913).

‡ *Ibid.*, 6, 67 (1904).

Gold-plating.—This is carried out in a bath containing 6 to 8 grams of gold per litre with an excess of potassium cyanide. Four volts is the normal E.M.F., the anodes being of gold in the form of very thin sheets. They exhibit passivity to a marked degree, and dissolve very slowly under normal current conditions.

Silver-plating.—A cyanide bath is always used, and contains about 22 to 25 grams of silver per litre. The current density should be about 3 amperes per square foot with an E.M.F. of 0.5 to 1.0 volt. The kathode efficiency is about 99 per cent., and the silver anodes dissolve readily. Little hydrogen is formed even at high current densities, and an excess of potassium cyanide increases the efficiency. As a rule, the electrolyte is prepared from silver chloride and potassium cyanide, the proportions of these constituents being such that the solution contains $\text{AgCN} + 3\text{KCN}$.

Chromium-plating.—Glaser * used a divided cell arrangement—an inner cell containing the chromium salt solution—and itself contained in an outer vessel, which held a mineral acid, or a solution of some salt, in which the anode was suspended. Using chromium chloride solution, containing 10 grams of metal per litre, the pure metal was obtained at 90 amperes per square foot, with an efficiency of 38.4 per cent. With chromium sulphate the best conditions were, at ordinary temperatures, 65 to 85 grams of metal per litre of solution, at a current density of 117 to 180 amperes per square foot. The efficiency was 84.6 per cent.

Sargent † worked with the usual single cell arrangement and used copper kathodes. Very good chromium deposits were obtained with chromic acid solutions, containing small amounts of chromium sulphate. A good deposit can be produced from a plating solution, containing 24.5 per cent. of CrO_3 and 0.3 per cent. of $\text{Cr}_2(\text{SO}_4)_3$ at a temperature of 20°C ., the current density being 10 amperes per square decimetre. A yield of 0.10 grams of chromium per ampere-hour may be obtained, under these conditions, with a voltage of a little over 3 volts and an electrode distance of about one inch.

Liebreich ‡ states that any impurity, even sulphuric acid, increases the tendency of chromium to form complex ions. For some unknown reason the chromium deposits adhere better when chromium sulphates, or sulphuric acid, is added to the chromic acid; sodium sulphate is still more advantageous. He § has pointed out that trivalent chromium ions are deposited from electrolytes which contain 16.5 per cent. by weight, and more, of

* *Zeits. Elektroc.*, 7, 656 (1901).

† *Trans. Amer. Electroc. Soc.*, 37, 479 (1920).

‡ *Zeits. Elektroc.*, 33, 69 (1927).

§ *Ibid.*, 34, 41 (1928).

H_2SO_4 . At lower concentrations of the sulphuric acid divalent chromium ions are deposited. Chromium plating has become very important recently, and Siemens * has summarised the present state of its production on a technical scale.

Iron deposition.—A number of solutions have been proposed for iron deposition, but few are of use. With few exceptions iron baths may be divided into two classes, chloride baths and sulphate baths. The chloride bath is composed of ferrous chloride 450 grams, anhydrous calcium chloride 500 grams, and water 750 cubic centimetres. The anodes dissolve well, and, working at current densities of about 120 amperes per square foot, the kathode efficiency is 95 per cent. For the sulphate bath Schlatter † suggests acid ferrous sulphate 150 grams, sodium sulphate 100 grams, and water one litre. No light is thrown upon what is meant by acid ferrous sulphate, but ordinary green vitriol may be used. He found that the bath must be maintained slightly acid. Herein lies one of the difficulties of working sulphate baths. They must be kept slightly acid if the best results are to be obtained, but any considerable acidity causes liberation of hydrogen, and thus leads to lower kathode efficiency. It is generally agreed that a sulphate bath must be worked at a raised temperature, and if a high current density is used, the temperature should be at least as high as 60° to 70° C.

Copper and brass-plating.—One copper bath contains about 25 grams of copper per litre, as KCuCN_2 , with 20 per cent excess of potassium cyanide, and the anodes are of pure sheet copper. The normal bath voltage is 3 to 4 volts and the current density 0.3 ampere per square decimetre. There is considerable hydrogen evolution at the kathode surface during the plating. Na_2SO_3 may be added to secure complete reduction of copper to the cuprous state and to avoid the production of poisonous cyanogen gas, which otherwise occurs. An addition of Na_2CO_3 ensures low hydrogen ion concentration.

The case of brass-plating is interesting from an electro-chemical point of view. As pointed out previously, a solution of zinc and copper complex cyanides contains complex anions, and in this case the electrode potentials of copper and zinc can be equalised, or, with a large excess of potassium cyanide, the zinc can actually be made more noble than the copper. With the depolarising alloy effect also coming in, it becomes possible to deposit alloys corresponding in composition and properties to commercial brasses. A suitable electrolyte bath for this purpose contains about 12

* *Zeits. Elektroc.*, 34, 264 (1928).

† German Patent, 309,271 (1917).

grams per litre each of copper and zinc present in $\text{KCu}(\text{CN})_2$ and $\text{K}_2\text{Zn}(\text{CN})_4$, with about 10 per cent. of KCN in excess. Anodes of rolled brass are used, and the bath is usually worked cold, taking 4 to 6 volts. The current density is variable, perhaps 0.35 ampere per square decimetre at the kathode, and still lower at the anode. There is marked evolution of hydrogen at the kathode.

157. Electrolytic extraction and refining of metals.—We shall now discuss briefly the refining of some metals by electrochemical processes.

Copper refining.—In the Marchese process * the anodes are cast from a mixture of copper, iron, lead and sulphur, in varying proportions. The electrolyte contains copper and iron sulphates, together with sulphuric acid. When a current is passed, the metallic constituents of the anode pass into solution and, at the kathode, copper is deposited, iron remaining in solution. This method is not very successful. A better one is that in which a copper sulphate solution is electrolysed, using insoluble anodes, lead or magnetite.

In the Laszczyński † process the filtered electrolyte contains about 3 per cent. of copper sulphate together with 1 per cent. of free acid, and much iron. The kathodes are of thin copper sheets, the anodes of lead. Using a current density of 0.5 to 1.0 ampere per square decimetre and 2.2 to 2.5 volts, copper can be reduced to 1 per cent. with a 90 to 95 per cent. efficiency.

Silver refining.—The crude material is cast and used as the anode, the bath containing mixtures of various nitrates with some free nitric acid. The various metals in the anode dissolve, and, at the kathode, the only metal likely to deposit, if appreciable quantities of silver are present, is copper, but this will only be deposited at high current density, high copper concentration and poor circulation of the electrolyte.

In the Moebius process ‡ the anodes are enclosed in a canvas diaphragm, and are arranged alternately with rows of kathodes, composed of fine silver foil. The concentration of the electrolyte is maintained at 15 to 20 grams of silver per litre, and 30 to 40 grams of copper per litre. With a current density of 4.4 amperes per square decimetre the electromotive force is 1.5 volts, approximately.

In the Balbach-Thum § process the cell is a shallow glazed porcelain trough, lined with graphite which acts as the kathode,

* *Zeits. Elektrochem.*, 1, 50 (1894). † *Electrochem. Ind.*, 5, 421 (1907).
 ‡ *Trans. Amer. Electrochem. Soc.*, 8, 125 (1905).
 § *Electrochem. Ind.*, 6, 277 (1908).

the anodes being arranged in shelves some distance above the kathode. Dietzel* used a cell in which the anolyte and katholyte † were separated by a horizontally arranged canvas diaphragm. The anolyte was drawn off from the bottom of the cell, passed over scrap copper, where the silver was deposited, and entered the cell by the kathode department. In the latter was the slowly rotating cylindrical kathode.

Gold refining.—The electrolyte is generally an AuCl_3 acid solution containing HAuCl_4 and HCl . At room temperature, and small anodic polarisation, the gold from the anode goes into solution. At high current density the metal becomes passive and chlorine is evolved, but the more acid there is present, the less easily does the passive state occur. When the metal dissolves, both auric and aurous chlorides are formed, although with higher current densities little aurous chloride is produced. If the cathodic polarisation is small, a reduction of the auric to the aurous salt occurs, with little gold deposition, but at higher polarisation, precipitation of the metal from the auric ions takes place. In practice, the gold anodes are suspended in an electrolyte containing 80 to 85 grams of gold per litre, and 30 per cent. of free HCl , with a trace of gelatine. The electrolysis is carried out at 70°F . with a current density of 15 to 17 amperes per square decimetre, and 0.6 to 0.8 volt. The silver is precipitated as the insoluble chloride, the lead by adding H_2SO_4 , while other impurities accumulate in the solution. As the gold content falls, AuCl_3 solution must be added to the electrolyte.

Nickel.—Since this metal is more electro-positive than hydrogen, and the cathodic overvoltage not very high, the metal cannot be deposited in large amounts from solutions containing much free acid, but during deposition the polarisation increases and a higher current density can be used. This is particularly the case with NiCl_2 solutions, and with acid solutions. A low concentration also increases the polarisation, but the lower limit is set by the necessity of preventing the appearance of basic salts.

In the Hopfner process ‡ the roasted ore is extracted by means of the spent anode liquors from the baths, and furnishes an electrolytic solution containing NiCl_2 and Cu_2Cl_2 . This is placed in a diaphragm cell with copper kathodes and carbon anodes. At the anodes the Cu_2Cl_2 is oxidised to CuCl_2 , and copper is deposited in the kathode department. The resulting liquor is then electro-

* *Zeits. Elektroch.*, 5, 81 (1899).

† The anolyte is the solution surrounding the anode, and the katholyte that at the kathode.

‡ *Chem. Zeits.*, 18, 1906 (1894).

lysed between sheet nickel kathodes and graphite anodes, giving nickel.

Zinc extraction.—Owing to the high cathodic overvoltage, zinc is deposited, even though it is more electro-positive than hydrogen, but if the electrolyte contains traces of copper, silver, or nickel, these metals will be deposited first, and afterwards there will be hydrogen evolution. An increase of current density, and a fall of temperature, both raise the overvoltage, so these conditions favour zinc deposition. A good bath contains 60 grams of zinc per litre, an acid concentration of 0.01 to 0.1 normal, and no impurities less electro-positive than zinc. The temperature should be low, and the current density, 1 to 2.5 amperes per square decimetre. The presence of the acid increases the conductivity of the electrolyte, and even with 150 to 200 grams of H_2SO_4 per litre, a high efficiency is obtained if the current density is high.

In the zinc chloride process the calcined ore is treated with CaCl_2 solution, and the liquor is slightly acidulated with HCl . The electrolyte is contained between graphite anodes and large revolving disc-shaped iron kathodes, the current density being 3 amperes per square decimetre at 5 volts.

Tin.—The scrap metal is made the anode in a caustic soda solution, and the dissolved metal deposited upon iron kathodes. The electrolyte is maintained at a concentration of 8 per cent. NaOH , at 70°F. , with a current density of 80 to 100 amperes per square metre, the voltage being 1.5 to 2.0 volts. Any iron present in the anode becomes passive, and does not dissolve, but the tin dissolves as stannous ions which are rapidly oxidised to tetravalent ions. In the electrolyte the latter form sodium stannate.

158. Fused electrolytes.—Molten salts are good conductors of electricity, and practically all types of inorganic compounds in the state of fusion have been subjected to electrolysis. Fused electrolytes and aqueous solutions seem to obey the same general laws of electrolytic conduction. Ohm's law and Faraday's law have been verified for molten electrolytes, when distorting influences are depressed.

Lorenz * summarised the following conditions as regulating the current yields at the kathode :—

(a) An increase in the temperature of fusion lowers the metal yield, and at the boiling-point none is deposited.

(b) The yield increases with the distance between the electrodes.

* *Zeits. anorg. Chem.*, 23, 97 (1900).

(c) The deeper an electrode is immersed in the fused electrolyte, the lower the yield seems to be.

(d) The factors which tend to lower the yield are :—

- (1) Mechanical losses.
- (2) Vaporisation of the metal by the use of too high a temperature.
- (3) The formation of lower compounds at the kathode.
- (4) The formation of higher compounds at the anode.
- (5) General secondary reactions.
- (6) The production of metallic clouds and fogs.
- (7) Thermal convection currents which mix the primary products of the electrolysis.

A few particular cases will now be considered. Aten, den Hertog and Westenberg* experimented with silver and copper in the form of halides. The salts were placed in a porcelain crucible, the kathode and anode consisting of the metal to be deposited. To measure the polarisation, they used a tube of pyrex glass, drawn down to a fine point and placed in the fused salt, close to the kathode; a wire of the metal being deposited was fixed in this tube. The voltage between the polarised kathode and this auxiliary electrode was then measured with a simple potentiometer. In all electrolytes the polarisation was small, but distinctly different with different anions, being greater for solutions of silver salts in fused alkali salts than for the pure fused salts. In this case we are dealing with a concentration polarisation, comparable with that in aqueous solutions, though much smaller because of the higher temperature.

Frary† refined aluminium by using a fused salt electrolyte, a process of importance since metallic aluminium cannot be deposited by the electrolysis of any aqueous solution. His type of cell was divided horizontally into two electrically insulated sections, the lower half containing a carbon bottom lining in which rested the molten alloy anode, A (Fig. 61). Upon this was the superposed molten bath layer, B, and upon the latter floated the molten aluminium kathode, C. The bath was composed of a mixture of cryolite, aluminium fluoride and barium fluoride, nearly saturated with alumina. The cell was easily started by pouring into it a layer of molten bath, several inches thick, and lowering the graphite electrodes so that they dip into the bath. A layer of molten alloy was then slowly poured in, followed by a layer of molten aluminium. To keep the cell operating, the aluminium produced at the kathode

* *Trans. Amer. Electroc. Soc.*, **47**, 265 (1925).

† *Ibid.*, 275 (1925).

must be tapped off, and a corresponding amount of impure aluminium, or aluminium-copper alloy, added to the anode. The cell operated with good current efficiency at 5 to 7 volts, and the metal obtained was about 99.90 per cent. pure.

Another important technical application of the electrolysis of fused electrolytes is the production of metallic magnesium.* In the chloride process $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is used as the raw material, and to prevent the salt from decomposing into magnesium oxide, it is mixed with an approximately equal part of NaCl . A cast-iron pot constitutes the electrolytic chamber, and serves as the kathode. A graphite anode is suspended in the fused salt, and is provided with a means of varying its depth in the electrolyte. The temperature range is 675° to 725° C., and although no separating diaphragm is

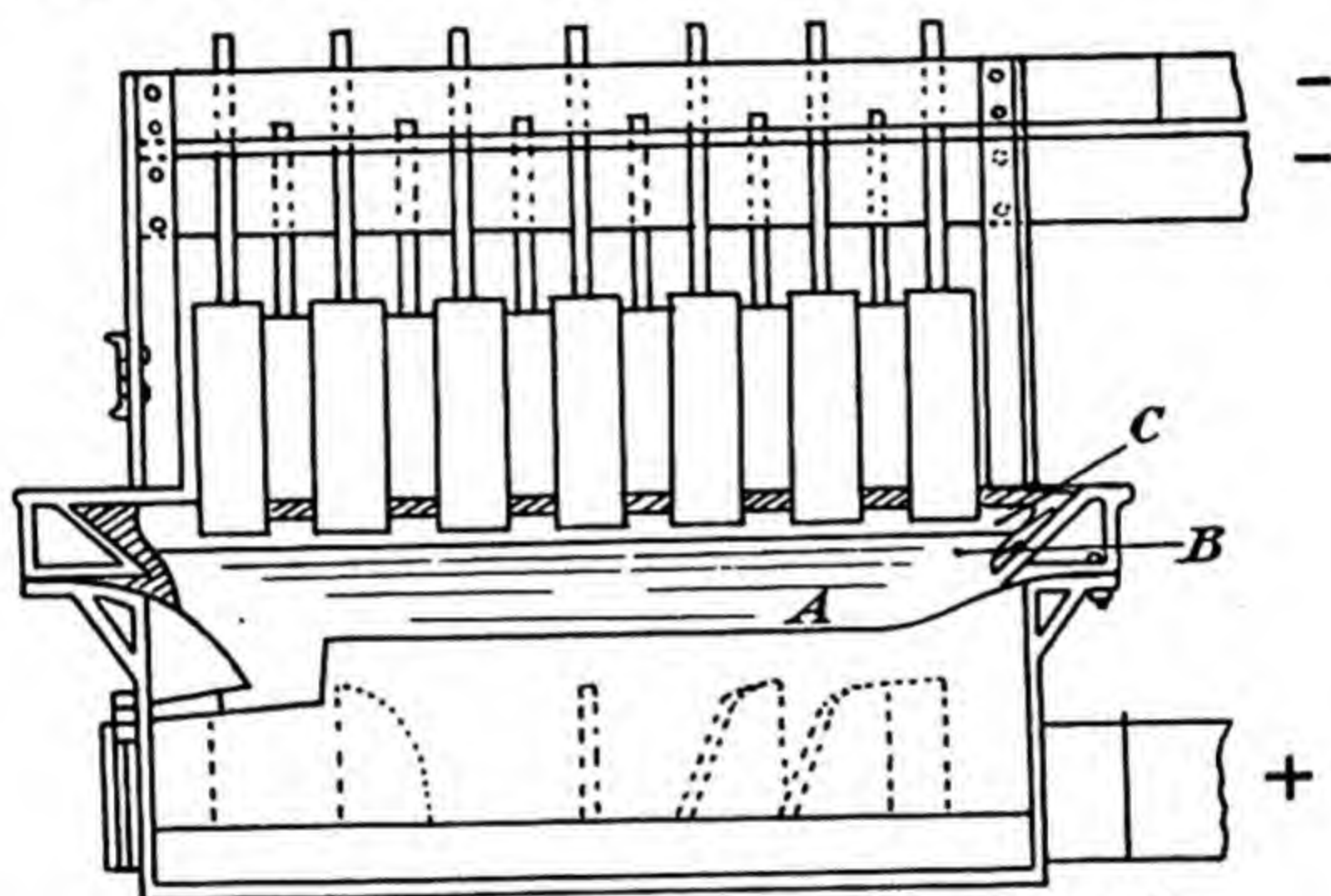


FIG. 61.—The aluminium fused electrolyte cell.

used, recombination between the magnesium and the chlorine is not excessive. Each pot takes 6 to 9 volts with a current density of 250 amperes per square decimetre of anode surface.

Magnesium can also be produced by the oxide process. The location of the anode is in the centre (Fig. 62), the cell consisting of a steel box with carbon anodes attached to copper bus bars. The kathodes are of cast iron, and project upwards through slots in the furnace shell. Magnesium does not alloy with iron, or steel, which makes that metal particularly suitable for the purpose. The electrolyte consists of magnesium and barium fluorides in equal parts, with sufficient sodium fluoride added to obtain the required fluidity at the operating temperature of 950° C. The oxide is

* See Harvey, *Trans. Amer. Electroc. Soc.*, 47, 327 (1925).

added to the bath around the anodes at frequent intervals, and as its solubility in the fluorides is less than 0.1 per cent., we have, primarily, an electrolysis of one of the fluorides with but little direct decomposition of the oxide.

As long as there is sufficient concentration of the magnesium salts around the negative electrodes, magnesium is reduced in the pure condition. Metallic fogs are encountered in this region, as might be expected from the high vapour pressure of the magnesium. The metal rises from the kathode, and collects just under the foreign crust of electrolyte. A kind of natural collecting chamber is thus formed. The product contains about 99 per cent. of metallic

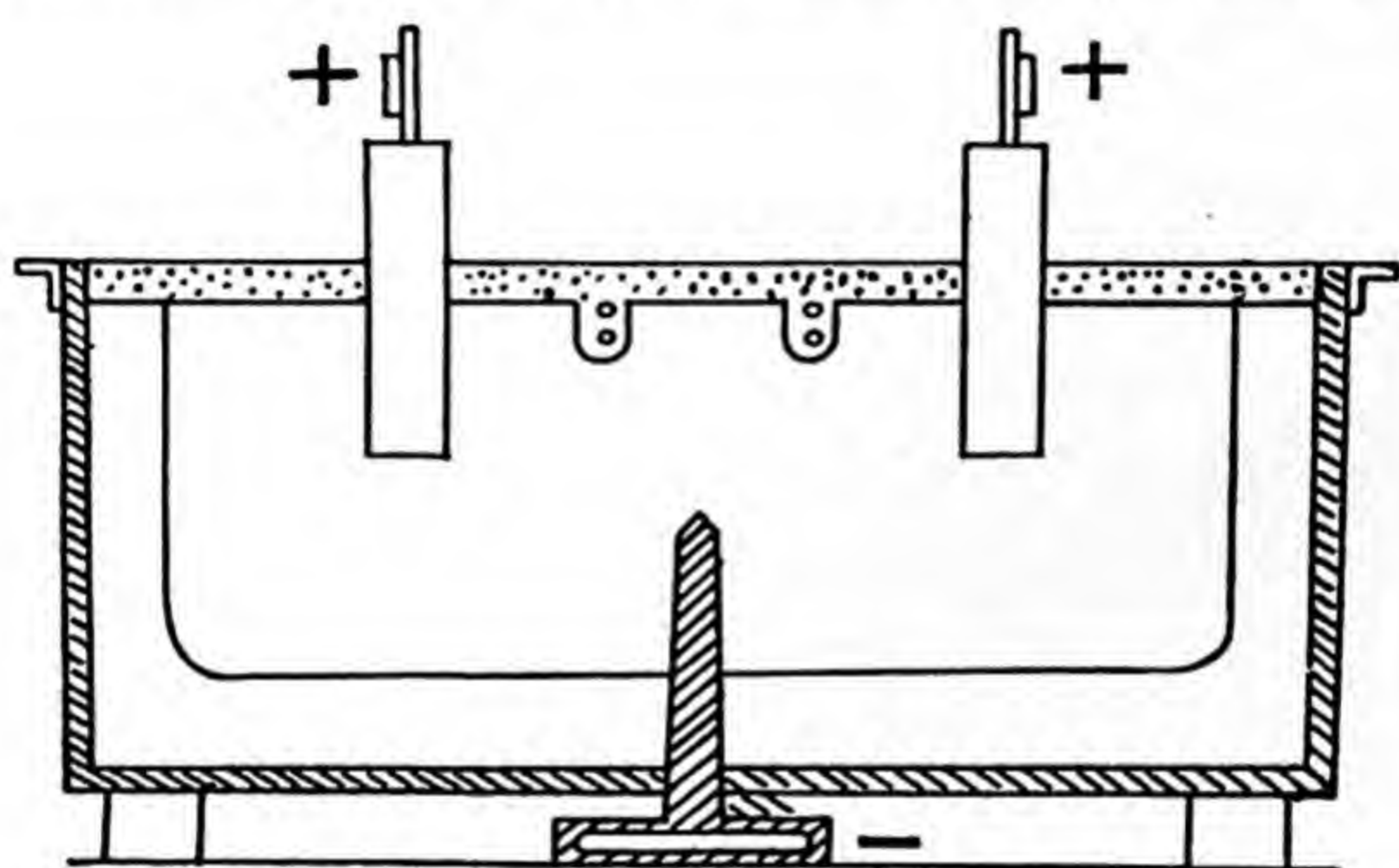


FIG. 62.—The magnesium oxide process cell.

magnesium, and furnaces of this type have been operated with 9,000 to 16,000 amperes at 9 to 16 volts.

Oxygen is formed at the anode as a result of the chemical action between the magnesium oxide and the nascent fluorine. If magnesium oxide is not added, or is not present in the fluoride bath, an electrolysis of the fluorides results, giving fluorine as the anode gas. The addition of magnesium oxide, although it is soluble only to 0.1 per cent., does act definitely as a depolariser, uniting with the fluorine at the anode, and lowering the voltage by continuously removing the anode gas film.

Metallic sodium is prepared from fused caustic soda, the most important methods being the Castner process and the contact electrode process. In the former the molten salt is contained in a cast-iron pot, A (Fig. 63), which is provided underneath with an extension, B, through which passes the kathode K, sealed into B by means of salt, which has solidified. The ring-shaped nickel anode, D, is hung from a flange on the top of the pot, and

between the electrodes is suspended a short cylindrical vessel, *E*, which, dipping beneath the liquid surface, forms a kathode chamber. It is continued below by means of an extension of fine wire gauze, which prevents globules of sodium from reaching the anode, since they are unable to pass through the meshes. The metal, liberated at the kathode, is ladled out by means of perforated spoons which retain the sodium and allow the molten salt to flow away.

Le Blanc and Brode * found that if commercial caustic soda is electrolysed, hydrogen and oxygen are produced at first, but as the electrolysis is continued, the hydrogen is evolved with greater

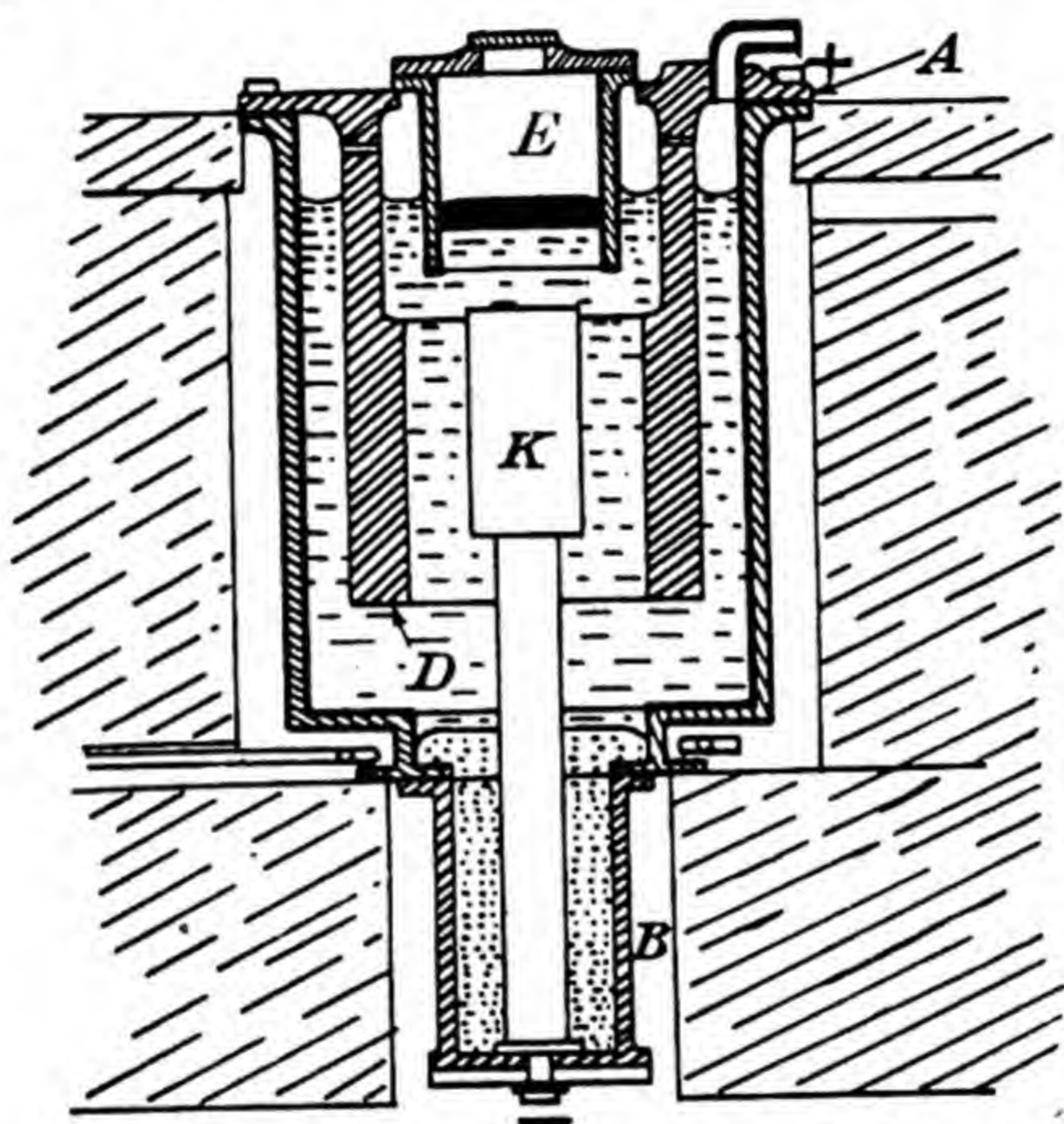


FIG. 63.—The Castner sodium cell.

difficulty, until, at a certain decomposition voltage, sodium is liberated. Previous dehydrating eliminates this hydrogen gas evolution.

The electrolysis is most conveniently carried out at a temperature of 315° to 320° C., but if higher temperatures are used, hydrogen and oxygen are both liberated at the anode, and explosions may result. The process is never more than 50 per cent. efficient.

Many attempts have also been made to obtain sodium by electrolysing sodium chloride, but since the pure salt melts at 803° C., and pure sodium boils at 877° C., the vapour pressure of the metal is

* *Zeits. Elektroc.*, 8, 717 (1902).

already high at 803°C . Ashcroft* used a double cell. In the first compartment chlorine is liberated on graphite anodes and sodium discharged into a molten lead kathode. The alloy is then impelled into the second compartment, containing fused caustic soda, where it forms the anode, and the sodium, passing to an iron kathode, overflows by a side pipe into a receiver.

Calcium may be obtained by the electrolysis of the fused

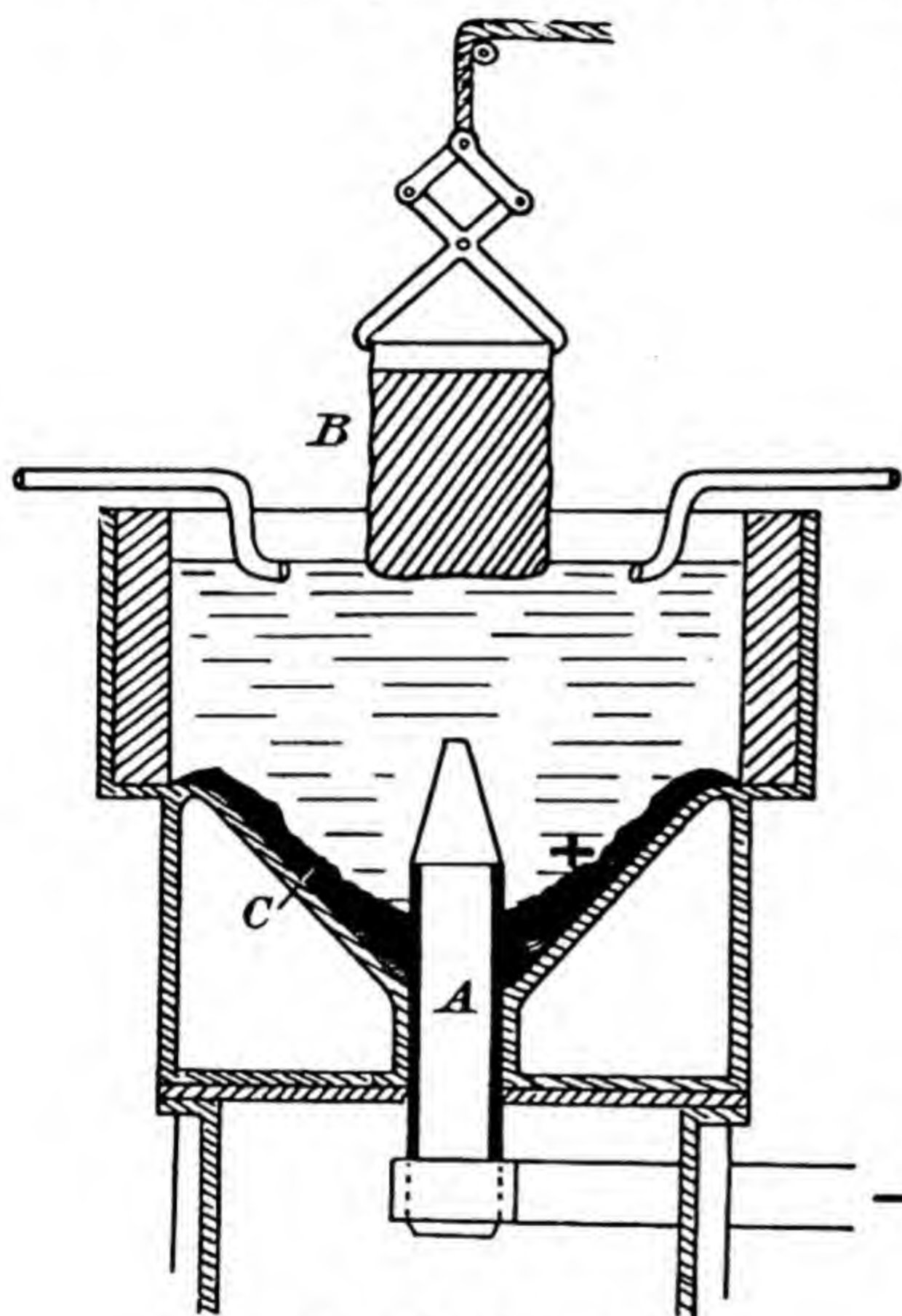


FIG. 64.—A calcium cell.

chloride which melts at 780°C ., although with impurities present its melting-point is less—probably about 750°C . The process now employed is illustrated in Fig. 64. The iron kathode, A, is fixed to the bottom of the tank, whilst the calcium, rising to the water-cooled region of the electrolyte, forms, in the manner indicated, a solid rod of the precipitated metal, B, which is continually removed by means of the gearing. The graphite anode, C, constitutes the side lining of the cell.

In a later cell of the Westinghouse Electric Company† the kathode is supported centrally, so that it dips into the

fused chloride, and is moved continuously upwards, carrying with it the adherent stick of metallic calcium, formed by a circular water-cooling arrangement round the kathode.

159. The anode effect.—A curious phenomenon often occurs during electrolysis of fused salts and is known as the *anode effect*.‡ During the course of electrolysis the voltage suddenly increases, the current decreases, a soft rustling hissing sound is heard, the

* *Trans. Amer. Electroc. Soc.*, 9, 123 (1906).

† United States Patent, No. 1,396,919 (1920).

‡ See Taylor, *Trans. Amer. Electroc. Soc.*, 47, 301 (1925).

anode appears to be covered with little luminous spark discharges, and the molten electrolyte, which up to this time had been in intimate contact with the anode, shrinks away from it and does not appear to meet it. The smooth, even, normal evolution of gas from around the anode has ceased. This is the anode effect, the electrode appearing to be entirely surrounded by a film of gas, and as the electrolyte is pushed away from the anode, small arcs form across the interface. Once this gas film has been established it tends to perpetuate itself, since the arcing generates an excessive amount of localised heat which causes the gas to expand. After the gas film has been established, there is a considerably higher voltage drop from the anode to the bath. The factors which interrupt regular, normal gas evolution at the anode, by causing the formation of this high resistance gas film, may be many in number. Any condition which tends to produce a local overheating on the surface of the anode may start a train of events which results in the anode effect. For example, a high resistance film of solid material may form on the anode surface, and this film may consist of impurities, left on the anode surface by the continued consumption of carbonaceous matter. It may consist of some relatively insoluble constituent of the electrolyte, which has migrated to the anode and adhered to it, or it may consist of solid electrolyte which has become attached to the anode, through the local cooling of the bath. As this high resistance film forms, the current density increases in other areas, and local overheating may start the formation of the anode effect at one or two points.

In general, the cause of the phenomenon may be attributed to any combination of conditions which permits of local overheating at any portion of the anode surface. This establishes the gas film at that point, and by thus diverting current to other parts of the anode area, which are already in a metastable state, overloads them and results in the practically instantaneous spread of the effect over the whole anode surface. The anode effect will disappear, of course, when the anode surface is cooled, or the current density reduced to such an extent that the gas film collapses, and normal evolution of gas is then resumed.

Kurt Arndt* investigated the difference in the behaviour of graphite and carbon electrodes in fused electrolytes. He found that when using the former, the critical current density for the anode effect was reached at 1.0 to 1.5 amps. per sq. cm., while with carbon it was 5 amps. per sq. cm. This fact should be taken into account when operating with fused electrolytes.

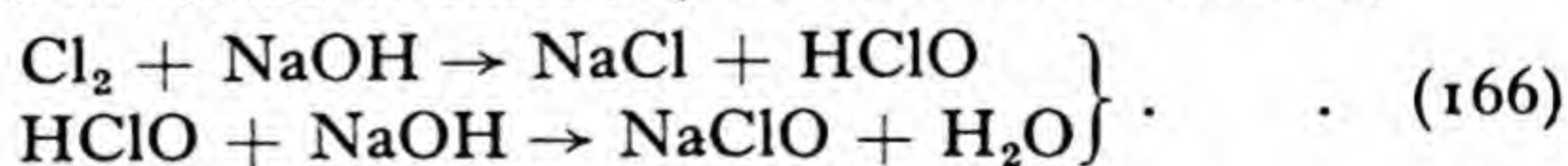
* *Zeits. Elektrochem.*, 22, 63 (1916).

160. The electrolysis of brine.—When a brine solution is electrolysed between electrodes of an indifferent metal, such as platinum or carbon, hydrogen ions are discharged at the kathode and chlorine ions at the anode. Now the normal sodium electrode potential has a high negative value -2.71 volts, so it is obvious that the hydrogen ions will be preferentially discharged, even from very strongly alkaline solutions. At the anode, since the normal electrode potential of the oxygen electrode, $O_2|OH^-$, is $+0.41$ volt, oxygen discharge from a neutral solution will commence at approximately $+0.82$ volt, if we take the concentration of hydroxyl ions in a neutral solution to be about 10^{-7} . Allowing for anodic overvoltage, oxygen will not be liberated below an anodic potential of about $+1.8$ volt, whereas the deposition potential of chlorine is, approximately, $+1.37$ volt for a normal NaCl solution. Therefore, we obtain as the primary products of this electrolysis caustic soda, together with hydrogen and chlorine as by-products. An apparatus which allows these substances to be collected separately is known as an *alkali-chlorine cell*. If the products are brought together, they will react, and according to the conditions prevailing, a hypochlorite or a chlorate solution is produced.

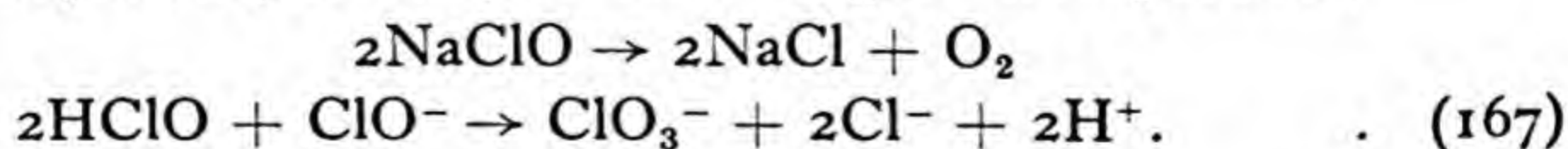
Chlorine, passed into water, reacts according to the equation,



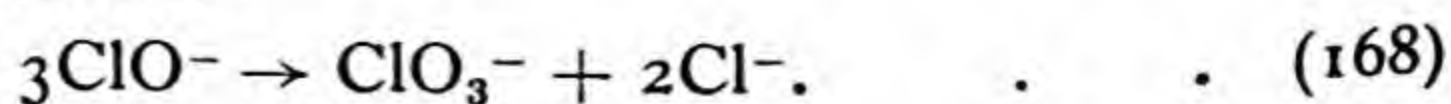
The HClO produced is practically unionised although, owing to the presence of hydrogen ions produced in equivalent quantity to the chlorine ions, the solution is acid. If caustic soda be used instead of water, such that two equivalents of the caustic alkali are present to a molecule of chlorine, we have the reactions,



and although the hypochlorite solutions in this form are fairly stable, they slowly decompose according to the equations,

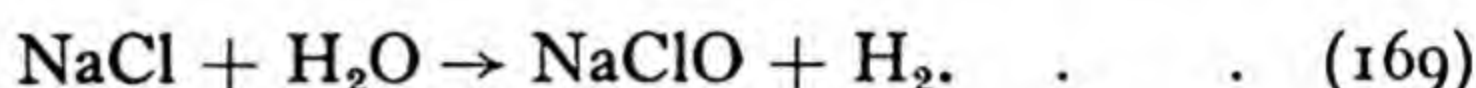


Solutions which contain ClO^- ions alone are stable, as also are solutions containing free HClO only, but when mixed they react according to equation (167). Then the hydrogen ions produced will at once regenerate HClO from the ClO^- ions, so that the concentration of the HClO will remain practically constant throughout, whilst that of the ClO^- ions decreases. Thus, we may say that the net result of the reaction is

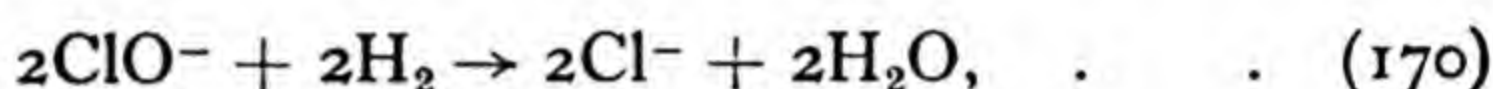


The presence of a small additional amount of HClO means a large relative increase in the HClO concentration and greatly accelerates the reaction given by equation (167). This may be effected by adding a little HCl , or slightly excess of chlorine, the HClO coming respectively from the ClO^- ions, or from the OH^- ions of the water. Such a solution will give the chlorate far more quickly than a solution prepared according to equation (166).

Hypochlorites.—In the preparation of hypochlorites brine is electrolysed without any diaphragm between inactive electrodes, the primary products of electrolysis reacting so that the result of passing 2 faradays of electricity through the cell is the reaction represented by

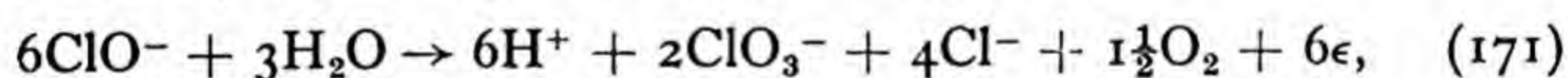


At the kathode the ClO^- ions are readily reduced by the nascent hydrogen thus,



and as the concentration of the NaClO rises, so does the rate of reduction, until in the end, the yield will fall to zero. This state of affairs may be avoided by adding, say, Na_2CrO_4 to the electrolyte. Apparently it forms a thin chromium-chromate diaphragm around the kathode, preventing the ClO^- ions from diffusing to the kathode surface.

The discharge of ClO^- ions at the anode will commence when their concentration reaches a certain value, and the reaction then occurring may be represented by the equation,



the H^+ ions combining with the OH^- ions, produced in equivalent amount at the kathode. As the anion discharge cannot be eliminated, a limit will be reached when the rate of disappearance of the hypochlorites, as given by equation (171), is equal to the rate of formation, as shown by equation (166). From equation (166) we see that the passage of 12 faradays of electricity produces 6ClO^- gram ions, whereas the passage of 6 faradays discharges 6ClO^- gram ions, producing 6 gram atoms of oxygen, associated in the chlorate and 3 gram atoms of gaseous oxygen, as shown in equation (171). Thus, at the steady state, there is a system of constant hypochlorite concentration, sodium chlorate being formed in increasing amounts at 66.6 per cent. current efficiency, the remaining 33.3 per cent. of the current producing gaseous oxygen.

Platinised-platinum anodes lower the deposition potential of chlorine ions and therefore suppress the discharge of hypochlorite

ions. A high NaCl concentration also means a smaller anodic polarisation, and thus a higher hypochlorite concentration before ClO^- discharge occurs. In general, we may say that the chief conditions to be observed in order to obtain a high yield of hypochlorite are: (a) a concentrated brine solution, (b) a low temperature and a high anode current density, (c) the presence of chromate in the bath, and (d) the use of platinised-platinum anodes.

161. Technical cells.—Bipolar electrodes are generally used in the cells because the number of exposed metallic connections is thereby reduced. Two forms of cells are typical of most, namely, the Kellner cell and the Haas-Oettel cell.

The former consists of a long cement trough open at the top and divided into a number of compartments by vertical glass partitions, these compartments communicating by channels, alternately, on each side. The bipolar electrodes are of platinum-iridium network. The cooled electrolyte circulates through the cell by gravity and there are thirty-six compartments in a 220 volt-60 ampere unit.

In the Haas-Oettel cell the electrodes are of carbon and the cell itself consists of an earthenware trough, open at the top, and divided into compartments by vertical plates of hard carbon, the current being led in and out by the end plates. Openings between the electrodes in the base of the trough allow cold brine to enter the cell, and when the current is started the rise in temperature and gas evolution cause

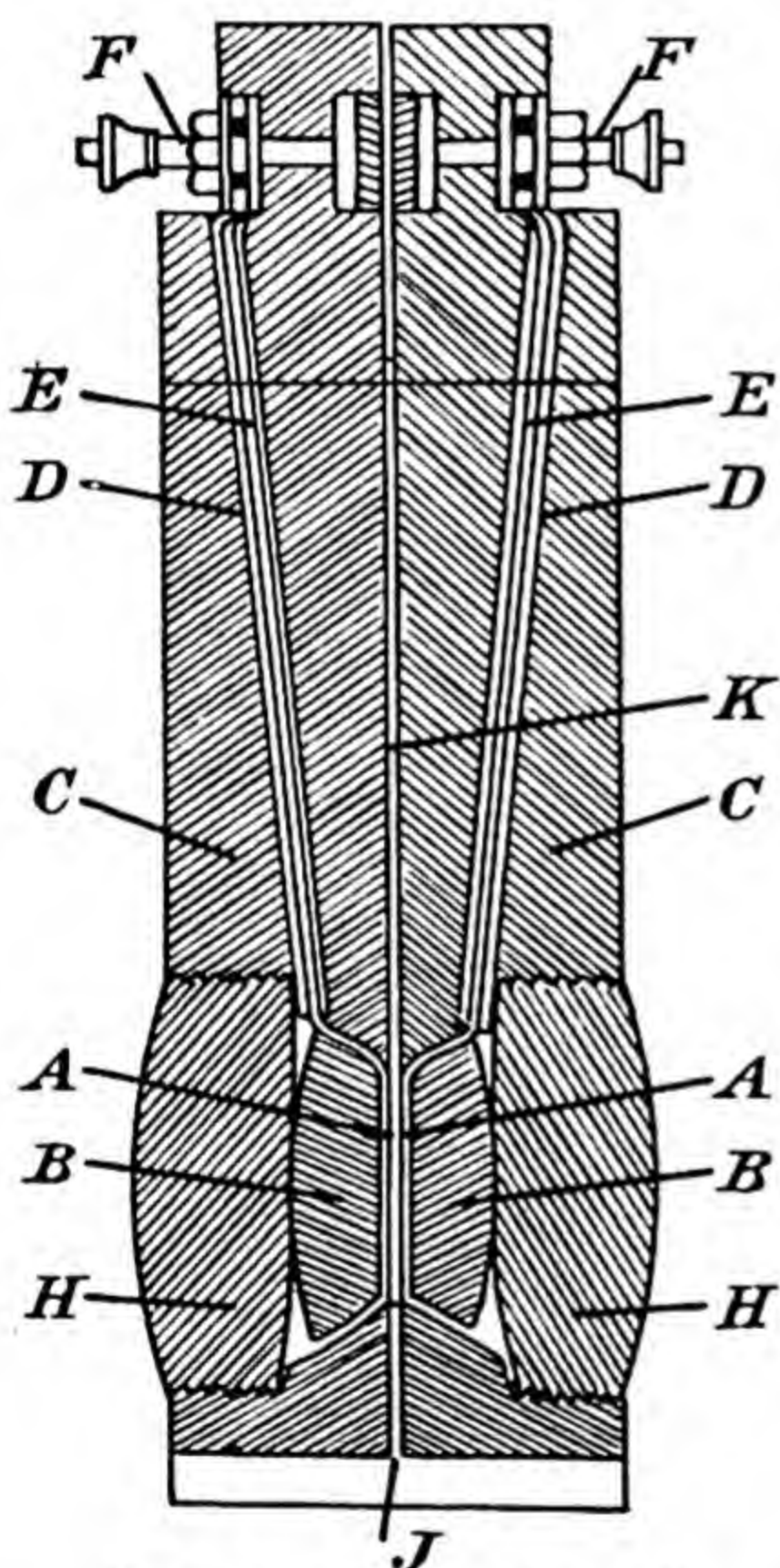


FIG. 65.—The platinode electrolyser.

the liquor to rise. The bleach liquor thus rises to the top and flows off, cooler brine entering beneath. In this manner the circulation is effected, and regulated, by electrolysis.

These cells have now been followed by improved types, such as the "platinode" electrolyser,* shown in Fig. 65. The platinum foil electrode, A, is backed with a vulcanite block, B, and inserted in

* See Hale, *Jour. Soc. Chem. Indus.*, **43**, 1291 (1924)

a dished recess in an ebonite plate, C. The foil is connected with a terminal, F, by means of a platinum wire, E, in the channel D. The electrode carrier shown is normally immersed in the electrolyte to the depth indicated by the horizontal line, and access of the electrolyte to the channel, D, is prevented by a filling, squeezed into position by the plug, H. Electrolyte circulates by the opening, J, at the bottom of the cell, through the channel K, and overflows through openings in the side on the level of the electrolyte.

Chlorate cells.—Chlorates may be formed in the two ways indicated in equations (167) and (171) and the two technical processes, based on these reactions, are termed the acid and the alkali process, respectively.

If the original solution is slightly acid, the formation of the chlorate is accelerated, and a rise of temperature to 70° C. also produces the same result. An addition of alkali chromate is beneficial, as it prevents cathodic reduction. With platinised-platinum electrodes a current efficiency of nearly 100 per cent. is obtained, as no oxygen is evolved at any stage.

In the alkali process the solution contains free alkali, and the ClO^- ion concentration, particularly at the anode, is increased. Thus its discharge begins at a lower hypochlorite concentration in the bulk of the solution than is the case when neutral brine is used. The current efficiency for the chlorate formation is never above 66 per cent. The conditions for successful operation of the alkali process are low temperature, polished platinum electrodes, fairly high current density, about 1.0 to 1.5 per cent. of NaOH in the brine, and some chromate to prevent cathodic hypochlorite reduction.

The acid process is carried out, as a rule, in long rectangular iron, or cement, cells, arranged in terraces, so that circulation is produced by gravity. A row of anodes is contained between two rows of kathodes, and a bath takes 1,000 to 1,500 amperes. The anodes are of smooth platinum-iridium alloy foil, and the kathodes of graphite, or iron. The voltage may vary from 4.5 to 5.5 volts with an anodic current density of 20 amps. per sq. dcm. Many types of cells have been used in practice.*

Alkali-chlorine cells.—We have already seen that by electrolysing a cold solution of brine and allowing the anode and kathode products to intermingle, there results a hypochlorite, or a chlorate, the actual product formed depending upon the conditions. We will now consider processes in which the chlorine and the alkaline solution are kept separated.

* See Gibbs, *Electrochem. Ind.*, 1, 11 (1902); French Patent, No. 283,737 (1904); United States Patent, No. 918,650 (1909).

The very high negative value of the deposition potential of sodium may be made more positive by employing a mercury, or lead, kathode with which the sodium alloys, or by using a metal on which the cathodic overvoltage is very high. In practice, sodium is liberated in the cell at a mercury kathode, the alkali amalgam being subsequently decomposed by water outside the cell.

As regards the anodes, they must withstand the action of the chlorine and are therefore made of platinum, carbon or magnetite, the platinum used being always smooth, never platinised. To obtain a good yield of chlorine the temperature should be low, and the current density high.

Concerning the cell design, the alkali must not reach the anolyte, and the various means adopted for preventing this afford a method of classifying the cells, the various types being commonly termed diaphragm, gravity and mercury cells, but this classification is entirely empirical. A few examples of these various cells will now be considered.

Diaphragm cells.—In the Hargreaves-Bird cell* (Fig. 66)

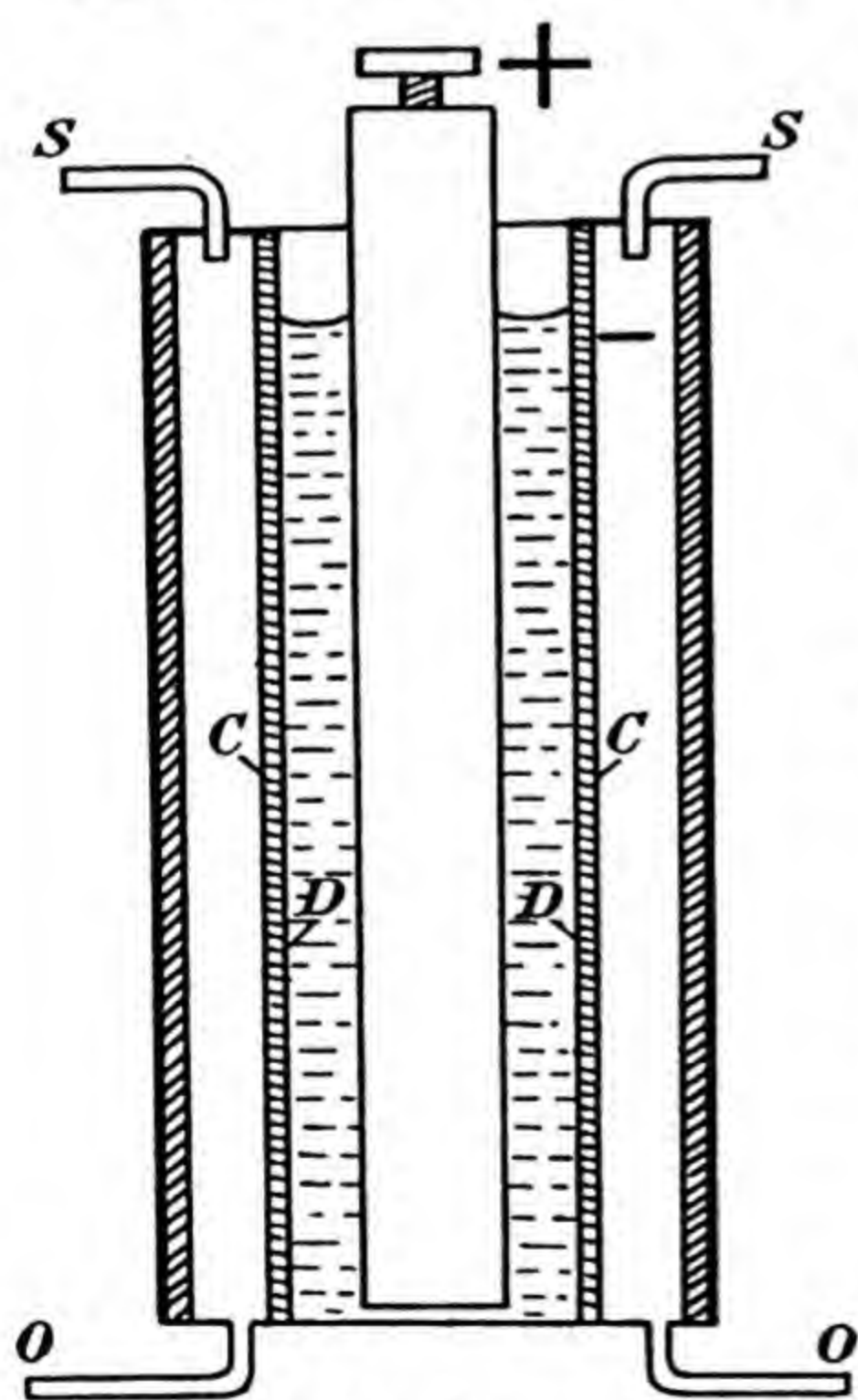


FIG. 66.—The Hargreaves-Bird cell.

a rectangular iron box, lined with cement, or in the place of iron, sandstone blocks clamped together, forms the containing vessel. The latter is divided longitudinally into three parts by two asbestos sheet diaphragms, D. The kathodes, C, are made of sheets of copper gauze of the same size as the diaphragms, and attached to them on the outside. The two kathode spaces between the copper kathodes and the sides of the cell are empty, except for steam and carbon dioxide, which pass into the top of the cell by way of the pipes, S, S. The anode compartment is filled with saturated brine which, during electrolysis, percolates through the diaphragm. Reaching the copper kathode, caustic soda is formed, and this is carried to the base of the cell by condensed steam and the carbon dioxide, and therefore leaves the cell by the pipes, O, O,

* See *Electrochem. Rev.*, 20 (1900); *Electrical World*, 46, 101 (1905).

as a sodium carbonate, or bicarbonate, solution, mixed with sodium chloride. The anodes are of graphite. The disadvantage of the cell is that it produces cheap soda crystals and soda ash, instead of comparatively high priced caustic alkali.

In the Townsend cell,* which is used in America, kerosene oil is employed in the kathode compartment to facilitate the rapid removal of the caustic soda from the kathode, so that diffused chlorine from the anode has little chance of converting it into the

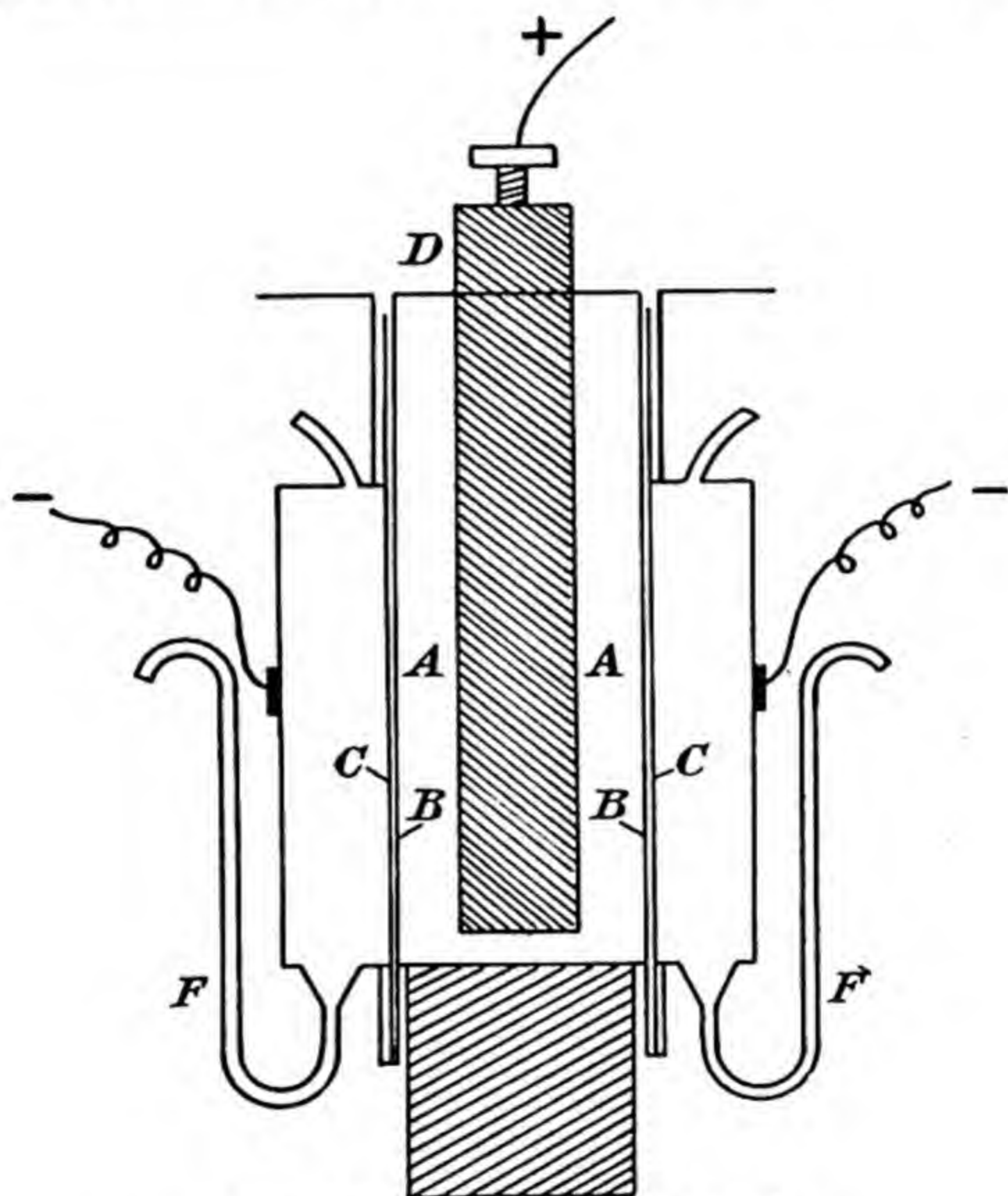


FIG. 67.—The Townsend cell.

hypochlorite, or chlorate. The centre compartment, A (Fig. 67), is the anode chamber, the sides of which are formed by asbestos diaphragms, B, on the outside of which press the iron grids, C, which serve as kathodes. The graphite anode, D, is cemented in through the roof of the anode compartment, the whole of this space being practically filled with the anode. The liquor between the anode and the kathode is partly converted into caustic soda, which passes through the diaphragm into the outer compartment. The electrolyte subsequently falls to the bottom of the kathode

* *Trans. Amer. Inst. Chem. Eng.*, 13, 1, 55 (1920).

compartment where it collects, and is ultimately drawn off by means of the outlet pipes, F, F. The current density is about 150 amps. per sq. ft. with 4 volts per unit. The electrodes are not more than one centimetre apart, and the diaphragm used is comparatively thin. It consists of woven asbestos cloth, painted with a mixture of asbestos fibre, Fe_2O_3 , and colloidal ferric hydroxide. By reducing the rate of percolation of the liquor through the diaphragm it is possible to obtain as much as 250 grams of NaOH per litre. The anodes are only very slowly attacked during electrolysis, and the loss of kerosene is negligible.

Among other diaphragm cells may be mentioned those of Billiter-Siemens,* Marsh,† Allen-Moore,‡ and Nelson.§

Mercury cells.—In mercury cells the alkali ions, and not the hydrogen ions, are deposited at the kathode, the liberated metal dissolving in the mercury. The amalgam thus formed is transferred to a separate compartment, where it is decomposed by water, the sodium being converted into the hydroxide. At the anode chlorine gas is evolved, and provided that the anodes are of good quality, and that the concentration of the alkaline halide is maintained, a pure gas results.

Actually the layer of electrolyte in contact with the mercury will be slightly alkaline, so that the reversible H^+ ion potential will be less than -0.4 volt, probably about -0.6 volt. The hydrogen cathodic overvoltage at the mercury surface, under the conditions existing, is, approximately, 1.35 volts, so that the total deposition potential for the hydrogen is about -2.0 volts, whereas, although the deposition potential of sodium from a solution of normal sodium ion concentration is -2.7 volts, the kathode potential necessary for sodium deposition at the amalgam surface is about -1.83 volts. Hence electrolysis discharges sodium in preference to hydrogen.

The anodes are of platinum, or carbon, and if smooth platinum is used, there is a high chlorine overvoltage, the anodic potential drop being probably about $+2.1$ volts, so that the voltage for the mercury cell seems to be about 4 volts.

By means of these mercury cells, concentrated soda liquor can be obtained, and a high current efficiency—about 95 per cent.—results. In addition, the purity of the caustic soda is high, approximately 99 per cent. Among the disadvantages is the production of hydrogen, arising from the interaction between the amalgam and the aqueous brine. Dangerous explosions have occurred as a

* *Trans. Farad. Soc.*, 9, 3 (1913); *Jour. Soc. Chem. Ind.*, 32, 993 (1913).

† *Trans. Amer. Electrochem. Soc.*, 39, 507 (1921).

‡ *Chem. Met. Eng.*, 21, 370 (1919).

§ *Trans. Amer. Electrochem. Soc.*, 35, 239 (1919).

result of this hydrogen content, and there is also the chance of the formation of HCl .

Taussig * has summarised the effects of various factors on the current efficiency of mercury cells. The chief results are as follows :—

- (i) The current efficiency is constant up to a certain amalgam concentration—0.01 per cent.—after which it falls off. This is true for a constant current density.
- (ii) The current efficiency depends upon the rate of circulation of the brine, and up to a certain point increases with it.
- (iii) The efficiency also increases with the current density, finally reaching a steady value.

Among the many types of mercury cells proposed may be mentioned the Solvay-Kellner type.† It was designed to take a large

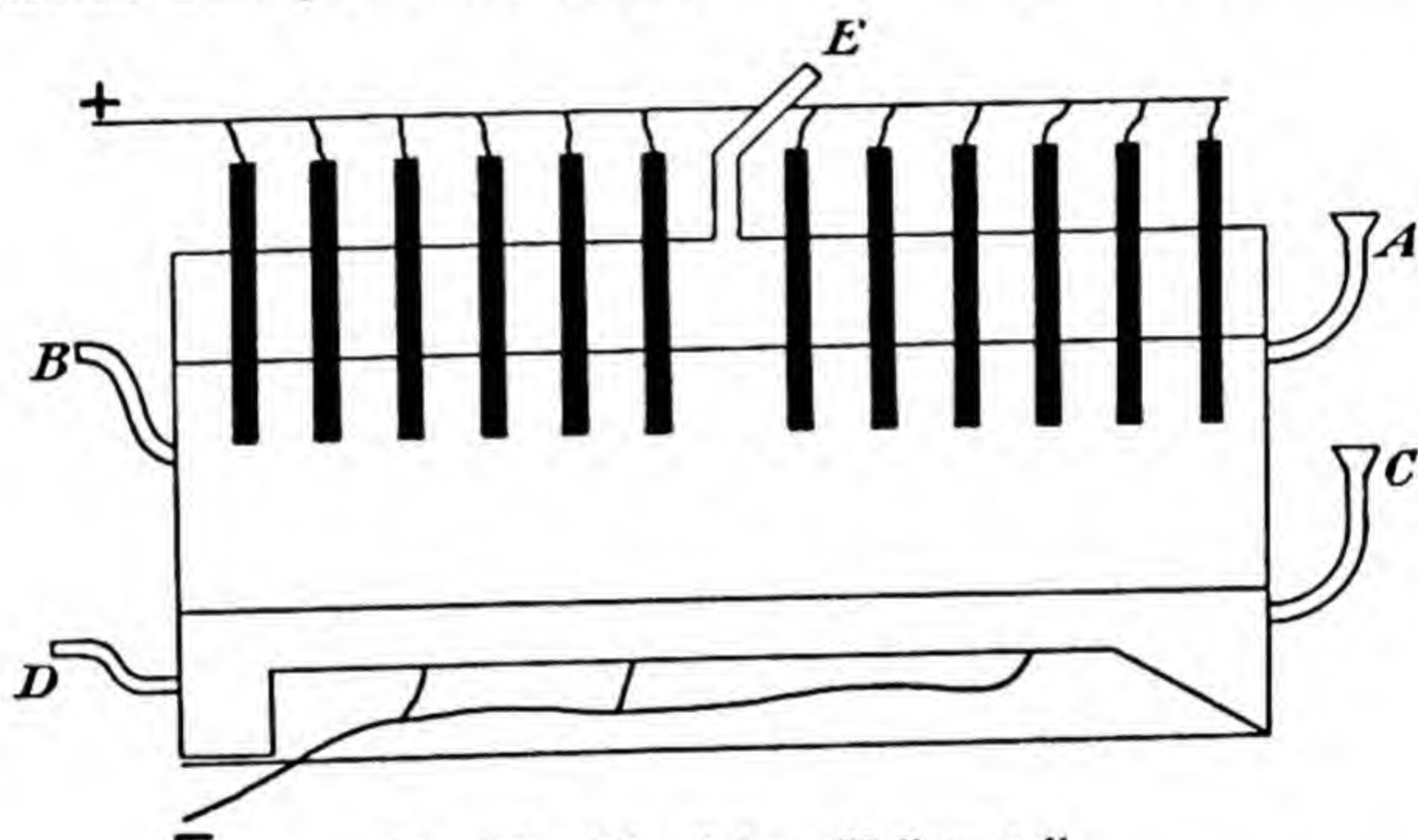


FIG. 68.—The Solvay-Kellner cell.

load, to work with the minimum of attention and to have a high output for its mercury content. The cell (Fig. 68) is stationary, and mercury flows through it by the action of gravity. A row of carbon anodes is arranged so that they dip into the brine solution, which enters at A, passes across the cell, during which it is decomposed, the resulting caustic liquor flowing out at B. The mercury enters at C and leaves by D, after giving up its sodium charge. Chlorine gas is drawn off by means of the pipe E. Thus, the streams of mercury and of brine flow in the same direction, the layer of mercury being a thin one, and its rate of flow is chosen so that an amalgam of suitable concentration leaves the cell. The

* See Askenasy, *Technische Elektrochemie*, II., 109 (1916).

† *Trans. Farad. Soc.*, 5, 258 (1910).

anodes are only 10 to 15 mm. above the mercury surface and the issuing amalgam flows, by gravity, into a separate trough, where it is decomposed by a counter-stream of water. The units are large, taking 10,000 to 15,000 amperes at a current density of 15 to 20 amps. per sq. dm.

Among the other mercury cells may be mentioned those proposed by Whiting,* Rhodin,† and Wildermann.‡ Although concentrated caustic liquors can be obtained from mercury cells, and their current efficiencies are high, there is the disadvantage of the initial cost of the mercury.

Gravity cells.—The chief characteristic of these cells is that the electrolyte moves and there is no diaphragm. Advantage is taken of the motion of the electrolyte, as a whole, to carry the caustic

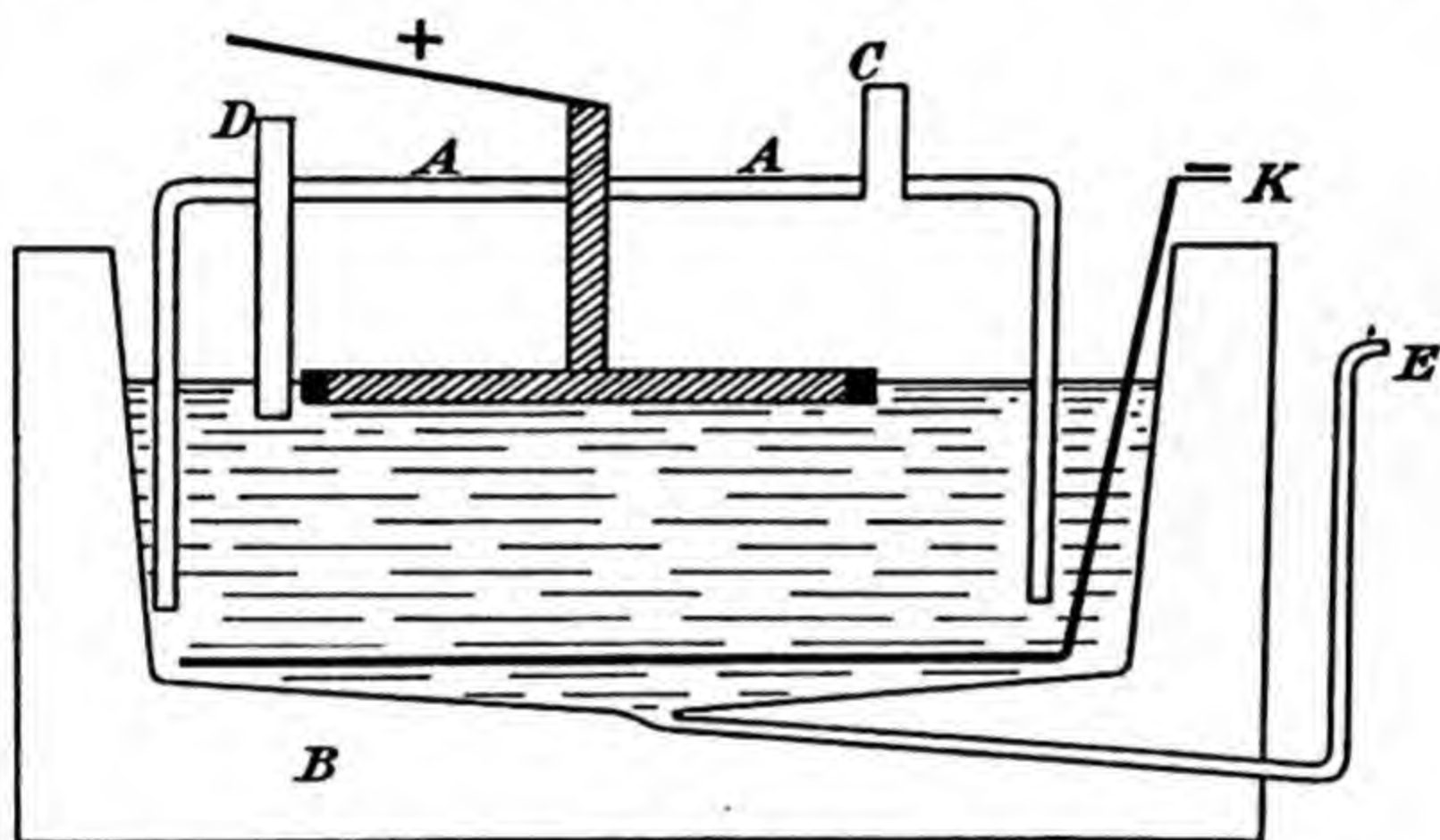


FIG. 69.—The Billiter-Leykam cell.

liquor away from the anode and prevent its contact with chlorine. In this way the effects of diffusion and ionic migration, which cause losses of alkali and chlorine, are largely counteracted by the flow of liquid.

In the Billiter-Leykam cell § a bell jar, A (Fig. 69), is inverted in an outer trough, B, and contains a chlorine outlet, C, D being an inlet for the brine. The anode of graphite is cemented into the bell, while the kathode, K, which is of iron, is T-shaped and is encased in asbestos to facilitate the removal of the hydrogen. Caustic soda falls to the bottom, and may be extracted through the pipe E. As the cell is fed automatically, it requires very little attention, and is found, in practice, to work smoothly and regularly. The

* *Trans. Amer. Electrochem. Soc.*, 17, 327 (1910).

† *Jour. Soc. Chem. Ind.*, 21, 449 (1902).

‡ *Trans. Amer. Electrochem. Soc.*, 22, 445 (1912).

§ English Patent, No. 11,693 (1910); *Trans. Farad. Soc.*, 9, 3 (1913).

current density used is 5 to 7 amps. per sq. dm. with a voltage 3.1 to 3.2 volts. The chlorine is very pure, and the cell is considered to be one of the most efficient non-mercury cells for producing caustic soda.

In the Acker process * the fused salt is electrolysed between carbon anodes and a molten lead kathode.

162. Other electrolytic processes.—In addition to the various substances already discussed, others are also prepared by electrolysis such as, for example, hydrogen and oxygen. Where both of these gases are required, *i.e.*, for the oxy-hydrogen flame, electrolysis is the most convenient method of preparing them. The technical electrolyzers usually employ solutions of NaOH, or KOH, and, as a rule, 2 to 2.4 volts form the normal working voltage. The purity of the gases reaches 99 per cent. for oxygen and 99.5 per cent. for hydrogen. Among the many types of cells used for this process may be mentioned that of Schuckert,† which consists of an iron trough, divided into a number of compartments, containing alternately iron anodes and kathodes. Iron hoods, suspended between the insulating partitions, carry off the gases. In the Jaubert ‡ cell (Fig. 70) five pairs of electrodes are connected in parallel, and each electrode is partly covered by a steel bell, A and B, in which the gases collect. The diameters of these bells and electrodes are proportional to the volumes of the gases evolved at each, but, as shown in the diagram, the lengths of the electrodes projecting below the bells are inversely proportional to the same gas volumes. The gases are allowed to flow out by means of the taps T_1 and T_2 . One unit takes 300 to 600 amperes at 2.3 to 2.5 volts.

The Knowles oxy-hydrogen cell § consists of an outer tank containing a number of sheet-iron gas collecting hoods in which are placed, alternately, the anodes and kathodes. The gas exits deliver into a pipe running across the bells. Later || ten of these cells were designed into a column cell for the purpose of reducing the floor space, occupied by the cells.

Various substances can also be produced by electrolysis of a suitable salt solution with an attackable electrode. If the electrolyte is a salt whose anion forms an insoluble salt with the anodic metal, for example, $PbSO_4$, it collects on the bottom of the bath beneath the anode. In this manner white lead, chrome yellow,

* *Electrochem. Ind.*, 4, 477 (1906).

† *Zeits. Elektrochem.*, 18, 169 (1912).

‡ See Hale, *Jour. Soc. Chem. Ind.*, 40, 122 (1921).

§ *Engineering*, 134, 315 (1922).

|| *Jour. Soc. Chem. Ind.*, 43, 119 (1924).

lead peroxide, cuprous oxide and lead hydrogen arsenate have been prepared.*

Bromine can be obtained by the electrolysis of concentrated bromide mother-liquors, containing a mixture of chloride and bromide.† Bromates are produced by the electrolysis of concentrated bromide solutions, containing a little alkali bichromate. The best working temperature is 40° to 50° C.

Percarbonates, hydroxylamine, hyposulphites, hydrogen per-

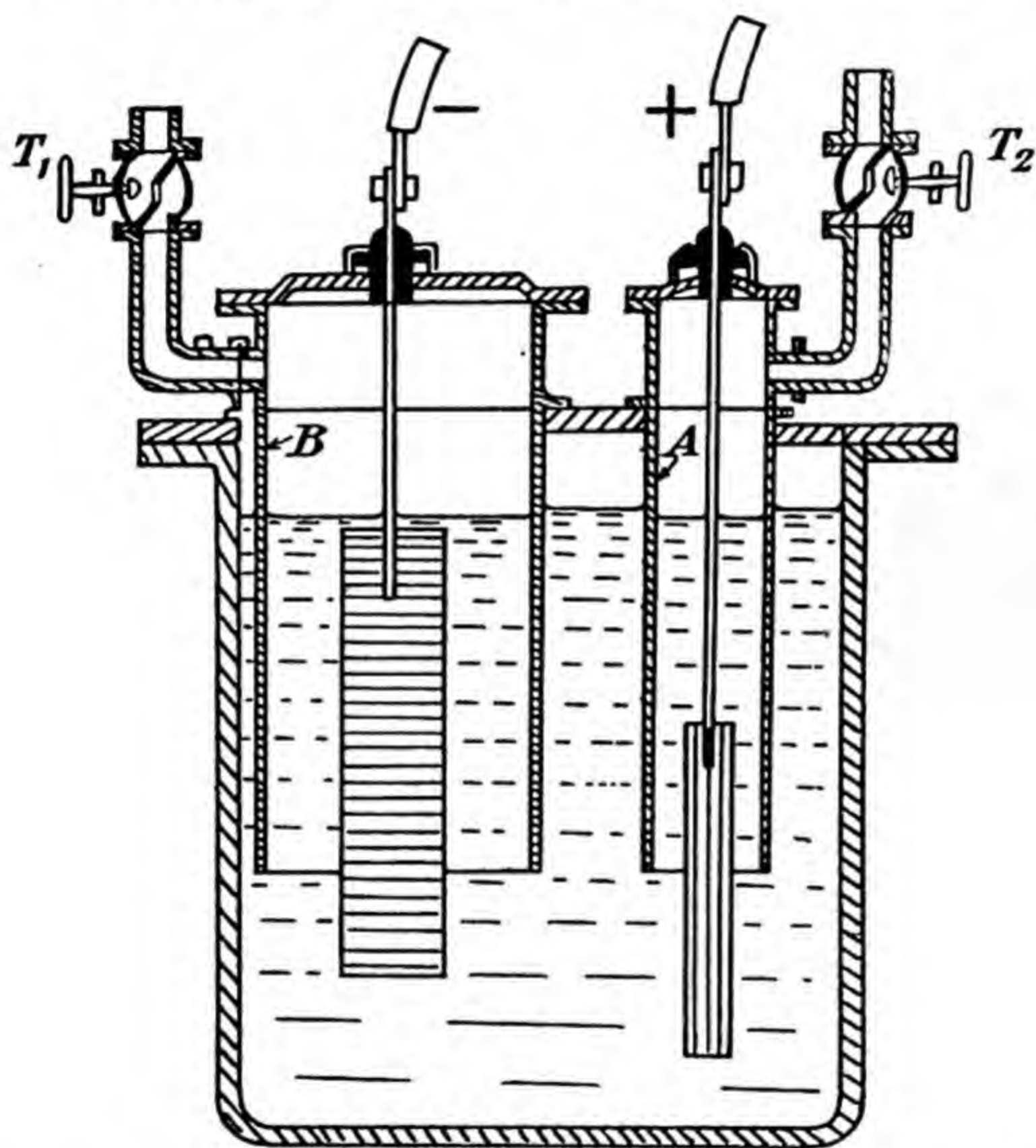


FIG. 70.—The Jaubert cell.

oxide, potassium permanganate, fluorine, iodoform, bromoform, anthraquinone, isopropyl alcohol, chloral, saccharine, potassium ferricyanide have all been prepared by electrolytic methods.

Although much work has been done on the preparation of organic compounds by electrolysis, it is evident that the full application of this phenomenon awaits development in many directions. This branch of electro-chemistry does not appear to have received the attention in this country which it deserves.

* See *Zeits. Elektroc.*, 9, 797 (1903); *Trans. Amer. Electroc. Soc.*, 5, 230 (1904); English Patent, No. 14,310 (1915).

† *Zeits. Elektroc.*, 16, 321 (1910).

BIBLIOGRAPHY.

- Allmand and Ellingham, Applied Electrochemistry.
 von Arsdale and Maier, Trans. Amer. Electrochem. Soc., 33, 109 (1918).
 Bancroft, Jour. Phys. Chem., 9, 277 (1905); 12, 36 (1908); Trans. Amer. Electrochem. Soc., 29, 309 (1916).
 Billiter, Zeits. Elektrochem., 33, 353 (1927).
 Bogitch, Comptes Rendus, 188, 328 (1929).
 Creutzfeldt, Zeits. anorg. Chem., 121, 25 (1921).
 Enos, Trans. Amer. Electrochem. Soc., 48, 37 (1925).
 Ferguson and Sturdevant, *ibid.*, 38, 167 (1920).
 Field, Trans. Farad. Soc., 5, 172 (1909).
 Fink and Pan, Trans. Amer. Electrochem. Soc., 43, 349 (1924).
 Frölich and Clark, Zeits. Elektrochem., 31, 649 (1925).
 Grube, Trans. Farad. Soc., 9, 216 (1914); Zeits. Elektrochem., 32, 561 (1926).
 Grube and Breitingner, *ibid.*, 33, 112 (1927).
 Grube and Reuss, *ibid.*, 27, 45 (1921).
 Hammond, Trans. Amer. Electrochem. Soc., 30, 103 (1916).
 Heidinger, Grube and Schlecht, Zeits. Elektrochem., 32, 70 (1926).
 Hineline and Cooley, Trans. Amer. Electrochem. Soc., 48, 61 (1925).
 Kern and Fabian, Electrochem. Ind., 6, 365 (1908).
 Kohlschutter, Zeits. Elektrochem., 30, 164 (1924).
 Müller, Phys. Zeits., 27, 778 (1926).
 Müller and Ekwall, Zeits. Elektrochem., 35, 84 (1929).
 Nichol and Watts, Trans. Amer. Electrochem. Soc., 48, 31 (1925).
 Paterson, Proc. Univ. Durham Phil. Soc., 4, 187 (1912).
 Riedel, Zeits. Elektrochem., 21, 5 (1915).
 Rollet, Comptes Rendus, 189, 34 (1929).
 Sanigar, Trans. Farad. Soc., 25, 1 (1929).
 Schischkin and Gernet, Zeits. Elektrochem., 34, 57 (1928).
 Schischkin, *ibid.*, 33, 83 (1927).
 Schoch, Amer. Chem. Jour., 41, 208 (1909).
 Spitzer, Zeits. Elektrochem., 11, 345 (1905).
 Stscherbakow and Essin, *ibid.*, 33, 245 (1927).
 Trans. Farad. Soc., 16, 1 (1921).

Title _____

Author _____

Accession No. _____

Call No. _____

**Borrower's
No.**

**Issue
Date**

**Borrower's
No.**

**Issue
Date**

APPENDIX I.

POISSON'S EQUATION.

CONSIDER a small rectangular parallelopiped of volume $\delta x \delta y \delta z$, bounded by the six plane faces, $x = x_0 \pm \frac{1}{2} \delta x$, $y = y_0 \pm \frac{1}{2} \delta y$, $z = z_0 \pm \frac{1}{2} \delta z$, and suppose that the whole space is charged with a continuous distribution of electricity of volume density ρ . Thus, the total electric charge enclosed by the six plane faces is $\rho \delta x \delta y \delta z$.

Let N_x denote the component of the electric force at the point x_0, y_0, z_0 , in the x direction, and ψ the electric potential at this point. Then,

$$N_x = - \left(\frac{\partial \psi}{\partial x} \right),$$

and the total normal induction outwards over the surface of area δS , which encloses the volume $\delta x \delta y \delta z$, is $\iint N \delta S$. The contribution to this amount from the face which lies in the plane $x = x_0 + \frac{1}{2} \delta x$ is equal to the area $\delta y \delta z$ multiplied by the mean value of N_x over the face, and may be written as

$$- \delta y \delta z \left[\frac{\partial \psi}{\partial x} + \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial x} \right) \frac{\delta x}{2} \right].$$

Similarly the contribution from the opposite face is

$$\delta y \delta z \left[\frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial x} \right) \frac{\delta x}{2} \right].$$

The sum of the contributions from the two faces perpendicular to the axis of x is therefore

$$- \delta y \delta z \delta x \frac{\partial^2 \psi}{\partial x^2}.$$

Hence considering the induction across the two other pairs of faces the whole value of $\iint N \delta S$ is, accordingly,

$$- \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \delta x \delta y \delta z.$$

But by Gauss's theorem the total normal induction across any closed surface is equal to 4π times the electric charge enclosed, *i.e.*,

$$\iint N \delta S = 4\pi \rho \delta x \delta y \delta z,$$

and, therefore,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -4\pi\rho. \quad (172)$$

This result is known as *Poisson's equation*. If the medium is of specific inductive capacity D , then,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi\rho}{D} \quad (173)$$

or, in vector notation,

$$\text{div. grad. } \psi = -\frac{4\pi\rho}{D} \quad (174)$$

where div. grad. is often denoted by the symbol ∇^2 .

APPENDIX II.

THE MOTION OF AN ION IN A SOLUTION.

As stated in section (146) Debye and Hückel deduced the relationship between the equivalent conductance and the concentration of an electrolyte by means of two general principles, namely, Boltzmann's law of distribution and Poisson's equation.

Consider an elementary volume δv in which the ionic concentration at any point at any instant may be represented by ϕ , where ϕ is a function of the co-ordinates, x, y, z . The number of ions within the volume is equal to $\phi(x, y, z, \delta v)$. In a given time τ some of the ions experience a fortuitous variation of their co-ordinates owing to the Brownian movements, so that if $d v$ is a very small volume within the volume δv , the number of ions within the latter at the end of the time τ is equal to

$$\left[\int \phi(x + \delta x, y + \delta y, z + \delta z) f \cdot d v \right] \delta v$$

where f is a function of the variations, $\delta x, \delta y, \delta z$, of the co-ordinates. Hence the increase in the number of ions within the volume δv during the time interval τ is

$$\left[\int \phi(x + \delta x, y + \delta y, z + \delta z) f \cdot d v - \phi(x, y, z) \right] \delta v.$$

Using Taylor's theorem, this increase is equal to

$$\left[\int \left(\delta x \frac{\partial \phi}{\partial x} + \delta y \frac{\partial \phi}{\partial y} + \dots + \frac{1}{2} (\delta x)^2 \frac{\partial^2 \phi}{\partial x^2} + \dots \right) f \cdot d v \right] \delta v.$$

Let
$$\bar{x} = \int \delta x \cdot f \cdot d v, \quad \bar{x}^2 = \int (\delta x^2) \cdot f \cdot d v, \text{ etc.,}$$

where \bar{x} denotes the total displacement along the x axis of all ions within the volume δv . Now since we are considering kinetic motion,

$$\bar{x} = \bar{y} = \bar{z} = 0; \quad \bar{x}\bar{y} = \bar{y}\bar{z} = \bar{x}\bar{z} = 0,$$

and suppose that $\bar{x}^2 = \bar{y}^2 = \bar{z}^2 = s^2$, where \bar{x}^2 denotes the total value of the squared displacements parallel to the x direction during the time interval, τ . The increase in the number of ions brought about by the kinetic motion is thus

$$\frac{s^2}{2} \left(\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} \right) \delta v, \text{ approximately,}$$

which, using vector notation,* may be written

$$\frac{s^2}{2} \text{div. grad. } \phi \cdot \delta \mathbf{v}.$$

An external electric intensity, X , may also produce a variation in the ionic distribution, and this force, acting upon an ion, will subject the latter to an electrical force, F . When steady motion is reached,

$$F = \zeta u,$$

u being the steady ionic velocity and ζ , a viscous, or retarding, force resulting from the viscous properties of the medium in which the ion moves. The number of ions within the volume $\delta \mathbf{v}$ will vary owing to the action of the electric force, and during the time interval, τ , the change in the number of ions will be equal to

$$- \tau \left(\frac{\partial u \phi}{\partial x} + \frac{\partial u \phi}{\partial y} + \frac{\partial u \phi}{\partial z} \right) \delta \mathbf{v},$$

i.e.,
$$- \tau \text{div. } \phi \frac{F}{\zeta} \cdot \delta \mathbf{v}.$$

Neglecting any movement of the liquid as a whole, we have for the total change in the number of ions,

$$\tau \frac{\partial \phi}{\partial t} \cdot \delta \mathbf{v} = \frac{s^2}{2} \text{div. grad. } \phi \cdot \delta \mathbf{v} - \tau \text{div. } \phi \frac{F}{\zeta} \cdot \delta \mathbf{v},$$

or
$$\tau \frac{\partial \phi}{\partial t} = \text{div. } \left[\frac{s^2}{2} \text{grad. } \phi - \frac{\phi F}{\zeta} \cdot \tau \right].$$

Now Einstein † has shown that

$$\frac{s^2}{2\tau} = \frac{kT}{\zeta},$$

where k is Boltzmann's constant, and T , the absolute temperature, so that

$$\zeta \frac{\partial \phi}{\partial t} = \text{div. } (kT \text{grad. } \phi - \phi F). \quad . \quad . \quad (175)$$

* We shall use the following vector notation :—

$$\text{rot}_x A = \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z},$$

$$\text{div. } A = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z},$$

$$\text{grad.}_x S = \frac{\partial S}{\partial x},$$

$$\text{and, div. grad. } S \text{ (denoted by } \nabla^2 S) = \frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2},$$

where A and S are vector and scalar quantities, respectively.

† *Ann. d. Phys.*, 17, 4, 549 (1905).

Suppose that the solution contains ions of various kinds, the number of the i th kind per c.c. being represented by n_i , and the charge on an ion of this kind by e_i . Further, suppose that under the influence of the external electric field the ions move along the x direction. The number of ions within the volume δv is

$$n_a \delta v + n_b \delta v + \dots,$$

and the electrical force acting upon an ion of the i th kind will be equal to

$$e_i X.$$

If ψ is the potential at the ion resulting from the ionic atmosphere, the electrical force acting upon the ion, due to the electric charge in this ionic atmosphere, is

$$- e_i \text{ grad. } \psi,$$

so that the total electrical force acting on the n_i ions is given by the expression

$$n_i e_i X - n_i e_i \text{ grad. } \psi.$$

Hence, from equation (175),

$$\zeta_i \frac{\partial n_i}{\partial t} = \text{div. } (kT \text{ grad. } n_i - n_i e_i X + n_i e_i \text{ grad. } \psi), \quad (176)$$

where n_i is written for the ionic concentration, ϕ . But from Poisson's equation (Appendix I.),

$$\text{div. grad. } \psi = - \frac{4\pi}{D} \sum n_i e_i, \quad (177)$$

and if we denote the co-ordinates of the position of an ion at any instant by x_0, y_0, z_0 , and its velocity by u_i , then,

$$x_0 - u_i t = x, \quad y_0 = y, \quad z_0 = z,$$

and

$$\frac{\partial}{\partial t} = - u_i \frac{\partial}{\partial x}.$$

Thus equation (176) becomes,

$$- \zeta_i u_i \frac{\partial n_i}{\partial x} = \text{div. } (kT \text{ grad. } n_i - n_i e_i X + n_i e_i \text{ grad. } \psi). \quad (178)$$

Putting $u_i = 0$ and $X = 0$ in this equation,

$$\text{div. } (kT \text{ grad. } n_i + n_i e_i \text{ grad. } \psi) = 0. \quad (179)$$

At great dilution grad. ψ is small, and we may write $n_i = \bar{n}_i$, i.e.,

$$n_i e_i \text{ grad. } \psi = \bar{n}_i e_i \text{ grad. } \psi.$$

Equation (179) reduces to

$$\text{div. } (kT \text{ grad. } n_i + \bar{n}_i e_i \text{ grad. } \psi) = 0,$$

which equation is satisfied by

$$n_i = \bar{n}_i - \frac{\bar{n}_i e_i \psi}{kT} \quad (180)$$

Also in equation (178) we may replace $-n_i e_i X + n_i e_i \text{ grad. } \psi$ by $-\bar{n}_i e_i X + \bar{n}_i e_i \text{ grad. } \psi$, when the solution is dilute, and putting

$$n_i = \bar{n}_i - \frac{\bar{n}_i e_i \psi}{kT} + \mu_i,$$

where μ_i is the deviation from the normal distribution, we have from equation (178),

$$\zeta_i u_i \frac{\bar{n}_i e_i}{kT} \cdot \frac{\partial \psi}{\partial x} = \text{div. } (kT \text{ grad. } \mu_i) = kT \text{ div. grad. } \mu_i, \quad (181)$$

and from equation (177),

$$\text{div. grad. } \psi = \frac{4\pi}{DkT} \sum \bar{n}_i e_i^2 \psi - \frac{4\pi}{D} \sum \mu_i e_i, \quad (182)$$

since $\text{div. } X = 0$ and $\sum \bar{n}_i e_i = 0$.

Let κ^2 be written for the term $\frac{4\pi}{DkT} \sum \bar{n}_i e_i^2$, which is the square of an inverse length, and if we denote the operation div. grad. by ∇^2 , we have from equation (182),

$$\nabla^2 \psi - \kappa^2 \psi = -\frac{4\pi}{D} \sum \mu_i e_i.$$

Substituting this result in equation (181),

$$\nabla^2 (\nabla^2 \psi - \kappa^2 \psi) = -\frac{4\pi}{DkT} \cdot \frac{u_i}{kT} \cdot \sum \bar{n}_i e_i^2 \zeta_i \frac{\partial \psi}{\partial x}. \quad (183)$$

We shall define ζ , the mean friction coefficient of the solution, by the relation

$$\zeta = \frac{\sum \bar{n}_i e_i^2 \zeta_i}{\sum \bar{n}_i e_i^2}, \quad (184)$$

and substitute w for the term $\frac{\zeta u_i}{kT}$, so that equation (183) becomes,

$$\nabla^2 (\nabla^2 \psi - \kappa^2 \psi) = -\kappa^2 w \frac{\partial \psi}{\partial x}. \quad (185)$$

Now it has been shown in section (146) that the total potential at a small distance, r , from an ion is $\frac{Ae^{-\kappa r}}{r}$ and thus,

$$\nabla^2 (\nabla^2 \psi - \kappa^2 \psi) = -\kappa^2 w \frac{\partial}{\partial x} \left(\frac{Ae^{-\kappa r}}{r} \right). \quad (186)$$

Since
$$\nabla^2 \left(\frac{A\epsilon^{-\kappa r}}{r} \right) = \frac{\kappa^2 A\epsilon^{-\kappa r}}{r},$$

we can put equation (186) in the form,

$$\nabla^2(\nabla^2\psi - \kappa^2\psi) = -\nabla^2 w \frac{\partial}{\partial x} \frac{A\epsilon^{-\kappa r}}{r},$$

or
$$\nabla^2\psi - \kappa^2\psi = -w \frac{\partial}{\partial x} \frac{A\epsilon^{-\kappa r}}{r} = -w \frac{\partial}{\partial r} \left(\frac{A\epsilon^{-\kappa r}}{r} \right) \cos \theta. \quad (187)$$

Let $\psi = R \cos \theta$, so that

$$\nabla^2\psi - \kappa^2\psi = \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dR}{dr} - \frac{2R}{r^2} - \kappa^2 R \right) \cos \theta.$$

Hence,
$$R = -\frac{wA\epsilon^{-\kappa r}}{2},$$

and a special solution of this equation is

$$\psi = -\frac{wA\epsilon^{-\kappa r}}{2} \cos \theta. \quad (188)$$

Thus, adding to this result a solution of the equation,

$$\nabla^2(\nabla^2\psi - \kappa^2\psi) = 0,$$

and putting it in a form containing $\cos \theta$, we obtain

$$\psi = \left(-\frac{wA\epsilon^{-\kappa r}}{2} + A' \frac{d}{dr} \frac{\epsilon^{-\kappa r}}{r} + A'' \frac{d}{dr} \frac{\epsilon^{\kappa r}}{r} + \frac{B'}{r^2} + B'' r \right) \cos \theta. \quad (189)$$

Now the potential ψ must decrease as the concentration becomes less, and, therefore,

$$A'' = 0 \quad \text{and} \quad B'' = 0.$$

Hence, the total potential close to an ion is given by

$$\psi = \frac{A\epsilon^{-\kappa r}}{r} + \left(-\frac{wA\epsilon^{-\kappa r}}{2} + A' \frac{d}{dr} \frac{\epsilon^{-\kappa r}}{r} + \frac{B'}{r^2} \right) \cos \theta. \quad (190)$$

Therefore, owing to the motion of the ion, an additional potential is created on the ion which is, approximately, equal to

$$\left[(-A' + B') \frac{1}{r^2} + \frac{\kappa^2 A' - wA}{2} + \left(\frac{wA}{2} - \frac{\kappa^2 A'}{3} \right) \kappa r \right] \cos \theta.$$

Since the ions are small compared with the radius, $\frac{1}{\kappa}$, of the ionic

atmosphere, $(-A' + B') \frac{1}{r^2}$ must be exceedingly small at great dilutions, and so $A' = B'$. There will be a null point near the ion at which the electric potential due to the ion and that due to the asymmetry of the ionic atmosphere are equal and opposite in sign so that these two

electrical charges thus constitute what may be termed an ionic dipole. Thus the potential which the latter exerts at any point is proportional to $\frac{\cos \theta}{r^2}$ and so $\frac{-wA + \kappa^2 A'}{2} = 0$,

$$\text{or} \quad A' = \frac{wA}{\kappa^2}. \quad (191)$$

$$\text{But from section (146),} \quad A = \frac{e_i}{D},$$

and, therefore, expanding equation (190) and putting in the values of the various constants,

$$\psi = \frac{e_i}{D} \cdot \frac{e^{-\kappa r}}{r} + \frac{w\kappa e_i}{6D} r \cos \theta, \text{ approximately.}$$

Hence, the potential of the ion due to the asymmetry of the ionic atmosphere is

$$\frac{w\kappa e_i}{6D} r \cos \theta,$$

or, since $w = \frac{\zeta u_i}{kT}$, the excess potential is given by

$$\frac{\zeta u_i \kappa e_i}{6DkT} r \cos \theta \quad \text{or} \quad \frac{\zeta u_i \kappa e_i}{6DkT} x.$$

Thus, the additional electric intensity at the ion, due to this asymmetry, and acting in a direction opposed to the applied electric force, is equal to,

$$\frac{\zeta u_i \kappa e_i}{6DkT}. \quad (192)$$

Since there is in each volume element of the solution an electric charge arising from the presence of the ionic atmosphere, and since the sign of this charge is opposite to that of the ionic charge, an electric force will act upon this volume when an external electric field is applied, the direction of this force being in the opposite direction to that acting upon the ion. As a result, the ion will experience a viscous force opposing its motion, which will be greater than would be the case in the absence of an ionic atmosphere. In other words, a correction must be applied to the retarding force, as obtained from Stokes's law.*

According to Poisson's equation, the density of the electricity within the ionic atmosphere is equal to $-\frac{D}{4\pi} \nabla^2 \psi$, and the force, F_1 , acting upon unit volume of the ionic atmosphere may be written thus:

$$F_1 = -\frac{DX}{4\pi} \nabla^2 \psi, \quad (193)$$

* See Stokes, *Collected Papers*.

where, as before, X is the applied electric force. In the case of a very dilute solution we have, from equation (185),

$$\nabla^2 \psi - \kappa^2 \psi = 0, \quad . \quad . \quad . \quad (194)$$

and, therefore,

$$F_1 = -\frac{DX}{4\pi} \nabla^2 \psi = -\frac{DX}{4\pi} \kappa^2 \psi. \quad . \quad . \quad (195)$$

If an incompressible liquid moves with a velocity v past an ion, the hydro-dynamical equations, formulated by Stokes,* give rise to the following results:

$$\eta \text{ rot. rot. } v = -\text{grad. } p + F_1, \quad . \quad . \quad (196)$$

$$\text{and} \quad \text{div. } v = 0, \quad . \quad . \quad . \quad (197)$$

where η is the coefficient of viscosity of the liquid, p , the pressure which it exerts and F_1 is given by equation (195). Taking the div. of equation (196) and utilising equation (197), we have

$$\nabla^2 p = \text{div. } F_1 = -\frac{DX}{4\pi} \nabla^2 \frac{\partial \psi}{\partial x}, \quad . \quad . \quad (198)$$

of which a solution is

$$p = -\frac{DX}{4\pi} \frac{\partial \psi}{\partial x}. \quad . \quad . \quad . \quad (199)$$

Adding this result to the general solution of the equation,

$$\nabla^2 p = 0,$$

the complete solution, expressed in polar co-ordinates, is

$$p = \left(A_0 + \frac{B_0}{r} \right) + \left(A_1 r + \frac{B_1}{r^2} - \frac{DX}{4\pi} \frac{\partial \psi}{\partial r} \right) \cos \theta, \quad . \quad (200)$$

in which A_0 , B_0 , A_1 and B_1 are constants, and $\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial r} \cos \theta$.

The angular velocity, ω , of the liquid at the surface of an ion, past which the liquid is moving, is related to v according to the equation,†

$$\omega = \text{rot. } v, \quad . \quad . \quad . \quad (201)$$

and, therefore, if we take the rot. of equation (196),

$$\eta \text{ rot. rot. } \omega = \text{rot. } F_1, \quad . \quad . \quad . \quad (202)$$

since $\text{rot. grad. } p = 0$.

Assuming that the liquid moves along the x direction, the components of v , namely, v_r and v_θ , will have definite values, but the third component, v_ϕ , is zero (Fig. 71). The three components of the angular velocity are determined explicitly from equation (201) and have the following values:

* *Loc. cit.*

† See Stokes, *Collected Papers*, or any book on Hydrodynamics.

$$\omega_r = \frac{1}{r \sin \theta} \cdot \frac{\partial}{\partial \theta} \sin \theta v_\phi - \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} v_\theta,$$

$$\omega_\theta = \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} v_r - \frac{1}{r} \frac{\partial}{\partial r} r v_\phi,$$

$$\omega_\phi = \frac{1}{r} \frac{\partial}{\partial r} r v_\theta - \frac{1}{r} \frac{\partial}{\partial \theta} v_r.$$

But as the impressed velocity is along the x axis,

$$\omega_r = 0; \quad \omega_\theta = 0;$$

and since

$$(\text{rot. rot. } \omega)_\phi = -\frac{1}{r^2} \frac{\partial^2}{\partial r^2} r \omega_\phi - \frac{1}{r^2} \frac{\partial}{\partial \theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \omega_\phi,$$

and

$$\text{rot.}_\phi F_1 = -\frac{\kappa^2 D X}{4\pi} \sin \theta \frac{\partial \psi}{\partial r},$$

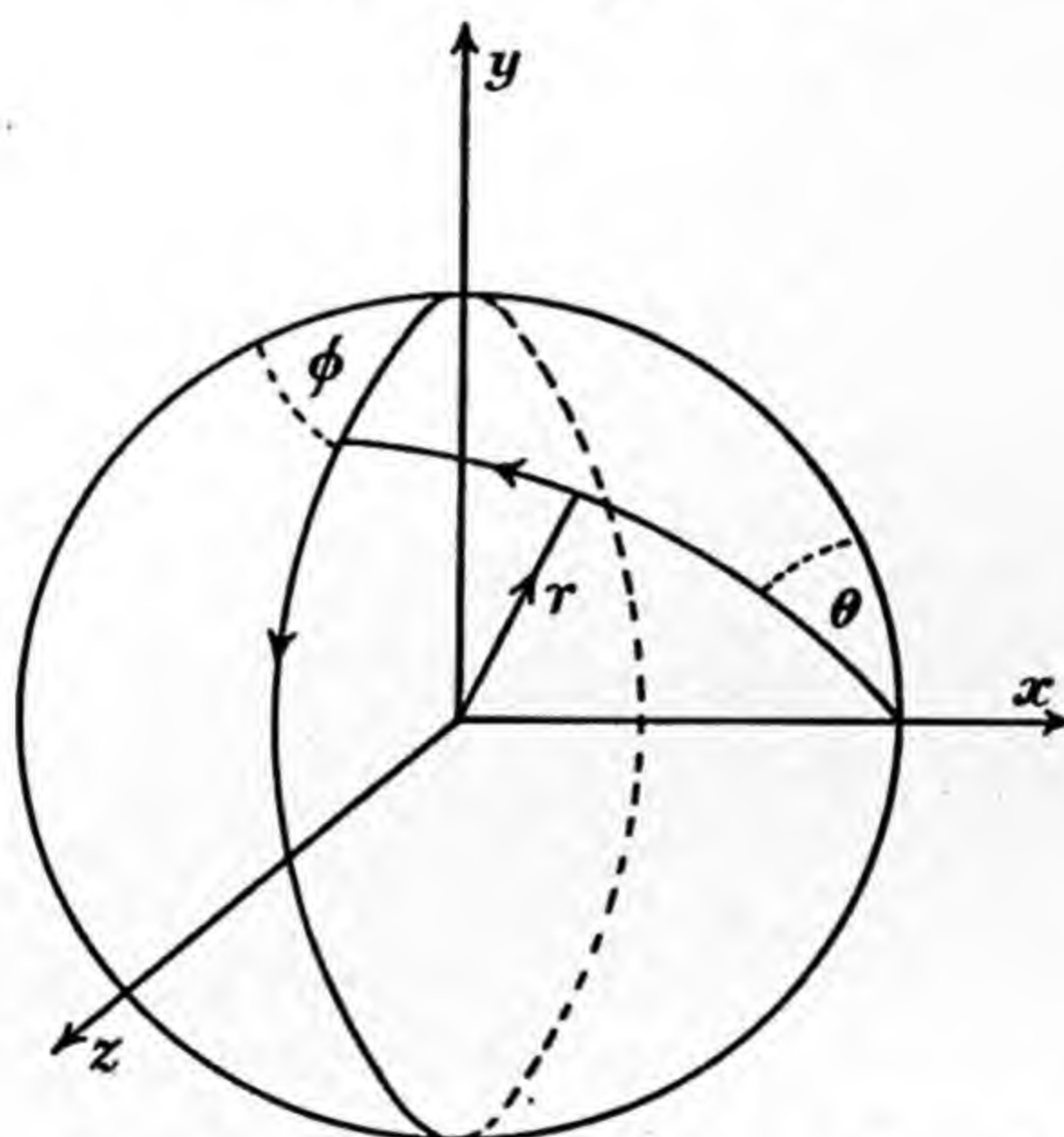


FIG. 71.—Ionic motion (polar co-ordinates).

we obtain from equation (202),

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} r \omega_\phi + \frac{1}{r^2} \frac{\partial}{\partial \theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \omega_\phi = -\frac{\kappa^2 D X}{4\pi \eta} \sin \theta \frac{d\psi}{dr}. \quad (203)$$

A solution of this equation is

$$\omega_\phi = \left(C_1 r + \frac{D_1}{r^2} - \frac{D X}{4\pi \eta} \frac{d\psi}{dr} \right) \sin \theta, \quad . \quad . \quad (204)$$

where C_1 and D_1 are constants to be determined.

Now equation (196) may be resolved into the three component equations, the ϕ component reducing to $0 = 0$. Hence, from the

r and θ component equations, and utilising equations (195), (196), (200) and (204), we have

$$\left(2\eta C_1 + 2\eta \frac{D_1}{r^3} - \frac{DX}{4\pi} \cdot \frac{2}{r} \cdot \frac{d\psi}{dr}\right) \cos \theta = \frac{B_0}{r^2} \\ + \left(-A_1 + \frac{2B_1}{r^3} + \frac{DX}{4\pi} \frac{d^2\psi}{dr^2}\right) \cos \theta - \frac{DX}{4\pi} \kappa^2 \psi \cos \theta,$$

and

$$\left(-2\eta C_1 + \frac{\eta D_1}{r^3} + \frac{DX}{4\pi} \cdot \frac{1}{r} \cdot \frac{d}{dr} r \frac{d\psi}{dr}\right) \sin \theta \\ = \left(A_1 + \frac{B_1}{r^3} - \frac{DX}{4\pi} \cdot \frac{1}{r} \cdot \frac{d\psi}{dr}\right) \sin \theta + \frac{DX}{4\pi} \kappa^2 \psi \sin \theta.$$

Comparing the coefficients of similar terms,

$$B_0 = 0, \quad C_1 = -\frac{A_1}{2\eta}, \quad D_1 = \frac{B_1}{\eta}.$$

Thus,

$$p = A_0 + \left(A_1 r + \frac{B_1}{r^2} - \frac{DX}{4\pi} \frac{d\psi}{dr}\right) \cos \theta, \quad (205)$$

$$\omega_\phi = \left(-\frac{A_1}{2\eta} r + \frac{B_1}{\eta r^2} - \frac{DX}{4\pi\eta} \cdot \frac{d\psi}{dr}\right) \sin \theta. \quad (206)$$

In addition, $\omega_r = 0$ and $\omega_\theta = 0$.

Since $\omega_\phi = \text{rot.}_\phi v$, we have from equation (206),

$$\left(-\frac{A_1}{2\eta} r + \frac{B_1}{\eta r^2} - \frac{DX}{4\pi\eta} \cdot \frac{d\psi}{dr}\right) \sin \theta = \frac{1}{r} \frac{\partial}{\partial r} r v_\theta - \frac{1}{r} \frac{\partial}{\partial \theta} v_r. \quad (207)$$

But $\text{div. } v = 0$, and, therefore,

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r) + \frac{1}{r \sin \theta} \cdot \frac{\partial}{\partial \theta} \sin \theta v_\theta = 0. \quad (208)$$

Let

$$v_r = R_1 \cos \theta \quad \text{and} \quad v_\theta = R_2 \sin \theta,$$

where R_1 and R_2 are functions of r . Thus, for equations (207) and (208) we may write

$$\frac{1}{r} \frac{d}{dr} (r R_2) + \frac{R_1}{r} = -\frac{A_1}{2\eta} r + \frac{B_1}{\eta r^2} - \frac{DX}{4\pi\eta} \frac{d\psi}{dr}, \quad (209)$$

and

$$\frac{1}{r^2} \frac{d}{dr} (r^2 R_1) + \frac{2R_2}{r} = 0, \quad (210)$$

i.e.,

$$r R_2 = -\frac{1}{2} \frac{d}{dr} (r^2 R_1). \quad (211)$$

Substituting this result in equation (209),

$$\frac{d^2}{dr^2} (r^2 R_1) - \frac{2}{r^2} (r^2 R_1) = \frac{A_1}{\eta} r^2 - \frac{2B_1}{\eta r} + \frac{DXr}{2\pi\eta} \frac{d\psi}{dr}. \quad (212)$$

A solution of this equation is

$$r^2 R_1 = \frac{A_1}{\eta} \frac{r^4}{10} + \frac{B_1 r}{\eta} + \frac{DX}{2\pi\eta\kappa^2} r \frac{d\psi}{dr},$$

since κ is equivalent to an inverse length. Adding the solution of the homogeneous equation, the complete solution is given by

$$r^2 R_1 = \frac{A_1}{\eta} \frac{r^4}{10} + \frac{B_1 r}{\eta} + A_3 r^2 + \frac{B_3}{r} + \frac{DX}{2\pi\eta\kappa^2} r \frac{d\psi}{dr},$$

where A_3 and B_3 are new constants. Hence equation (210) gives

$$r R_2 = -\frac{A_1}{2\eta} \cdot \frac{2}{5} r^3 - \frac{B_1}{2\eta} - A_3 r + \frac{B_3}{2r^2} - \frac{DX}{4\pi\eta\kappa^2} \frac{d}{dr} \left(r \frac{d\psi}{dr} \right).$$

Thus, since $v_r = R_1 \cos \theta$ and $v_\theta = R_2 \sin \theta$,

$$v_r = \left(\frac{A_1}{\eta} \cdot \frac{r^2}{10} + \frac{B_1}{\eta r} + A_3 + \frac{B_3}{r^3} + \frac{DX}{2\pi\eta\kappa^2} \cdot \frac{1}{r} \cdot \frac{d\psi}{dr} \right) \cos \theta, \quad (213)$$

$$v_\theta = \left(-\frac{A_1}{2\eta} \cdot \frac{2}{5} r^2 - \frac{B_1}{2\eta r} - A_3 + \frac{B_3}{2r^3} - \frac{DX}{4\pi\eta\kappa^2} \cdot \frac{1}{r} \cdot \frac{d}{dr} \left[r \frac{d\psi}{dr} \right] \right) \sin \theta, \quad (214)$$

$$v_\phi = 0.$$

$$p = A_0 + \left(A_1 r + \frac{B_1}{r^2} - \frac{DX}{4\pi} \frac{d\psi}{dr} \right) \cos \theta. \quad (215)$$

If u is the velocity of an ion moving through the liquid, we may impress on the system a negative velocity $-u$, so that the ion is brought to rest, and the liquid then streams past it. The forces acting upon the ion in the two cases are equal, and, therefore, assuming that the velocity of the liquid far removed from the ion is parallel to the x axis and equal to $-u$,

$$v_r = -u \cos \theta; \quad v_\theta = u \sin \theta.$$

Comparing these values with those given by equations (213) and (214), we see that

$$A_1 = 0, \quad A_3 = -u.$$

At the surface of the sphere of radius b , v_r and v_θ must vanish, and thus from equations (213) and (214),

$$\frac{B_1}{\eta} \cdot \frac{1}{b} + B_3 \left(\frac{1}{b} \right)^3 = u - \frac{DX}{2\pi\eta\kappa^2} \left(\frac{1}{r} \cdot \frac{d\psi}{dr} \right)_{r=b} \quad (216)$$

$$\frac{B_1}{\eta} \cdot \frac{1}{b} - B_3 \left(\frac{1}{b} \right)^3 = 2u - \frac{DX}{2\pi\eta\kappa^2} \left(\frac{1}{r} \frac{d}{dr} r \frac{d\psi}{dr} \right)_{r=b} \quad (217)$$

Hence,

$$\frac{B_1}{\eta} \cdot \frac{1}{b} = \frac{3}{2}u - \frac{DX}{4\pi\eta} (\psi)_{r=b}, \quad (218)$$

and

$$B_3 \left(\frac{1}{b} \right)^3 = -\frac{1}{2}u + \frac{DX}{4\pi\eta} \left(\frac{d^2\psi}{d(\kappa r)^2} \right)_{r=b} \quad (219)$$

We can now calculate the stress over the whole ionic surface, assuming that the sphere is transported by the force in the x direction. The components of the stress, p , across the surface of a sphere of radius r may be denoted by p_{rx} , p_{ry} , p_{rz} , and the conditions for no slipping of the liquid at the surface, $r = b$, give, when integrated over the surface of area S ,

$$\int p_{ry} dS = 0, \quad \text{and} \quad \int p_{rz} dS = 0.$$

Also,
$$p_{rx} = p_{xx} \frac{x}{r} + p_{yx} \frac{y}{r} + p_{zx} \frac{z}{r}, \quad (220)$$

where
$$p_{xx} = -p + 2\eta \frac{\partial v_x}{\partial x},$$

$$p_{yx} = \eta \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} \right),$$

$$p_{zx} = \eta \left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right).$$

In addition,

$$\begin{aligned} v_x &= v_r \cos \theta - v_\theta \sin \theta, \\ v_y &= (v_r \sin \theta + v_\theta \cos \theta) \cos \phi, \\ v_z &= (v_r \sin \theta + v_\theta \cos \theta) \sin \phi. \end{aligned}$$

We can calculate p_{rx} from equation (220), using the determined values for v and p from equations (213), (214) and (215), so that when $A_0 = 0$, we have

$$p_{rx} = B_3 \frac{3}{r^4} + \frac{DX}{4\pi\eta\kappa^2} \frac{d^3\psi}{dr^3} - \left\{ \frac{B_1}{\eta} \frac{3}{r^2} + B_3 \frac{9}{r^4} - \frac{6DX}{4\pi\eta\kappa^2} \left(\frac{1}{r} \frac{d^2\psi}{dr^2} - \frac{1}{r^2} \frac{d\psi}{dr} \right) \right\} \cos^2 \theta.$$

The force, acting on the sphere of radius r in the x direction, is $\int p_{rx} dS$, and is given by

$$\int p_{rx} dS = 4\pi\eta \left(-\frac{B_1}{\eta} + \frac{DX}{4\pi\eta} r^2 \frac{d\psi}{dr} \right).$$

The value of B_1 is obtained from equation (218), and, therefore, putting $r = b$,

$$\int p_{rx} dS = -6\pi\eta ub + DXb \left(\frac{d}{dr} [r\psi] \right)_{r=b};$$

but

$$\psi = \frac{e \cdot \epsilon^{-\kappa r}}{Dr},$$

and so the retarding, or viscous, force acting upon an ion of the i th kind, as it moves through the liquid, is

$$6\pi\eta u_i b_i + e_i X b_i \kappa, \text{ approximately.}$$

It has been shown—expression (192)—that the value of the retarding electrical intensity, due to the asymmetry of the ionic atmosphere, is equal to $\frac{e_i \kappa \zeta u_i}{6DkT}$, and thus the total accelerating electrical force acting upon the ion is

$$e_i X - \frac{e_i^2 \kappa \zeta u_i}{6DkT}.$$

Hence for steady ionic motion,

$$e_i X - \frac{e_i^2 \kappa \zeta u_i}{6DkT} = 6\pi\eta u_i b_i + e_i X b_i \kappa,$$

an expression utilised in section (146).

NAME INDEX.

(The numbers refer to pages.)

- A**BBOTT, 72.
 Abegg, 216, 236, 255.
 Acker, 409.
 Acree, 197, 320, 322, 335.
 Adams, 147, 283, 304, 355.
 Adler, 255, 294.
 Akashi, 275.
 Akerlöf, 220, 357, 378.
 Allen, 187, 310, 406.
 Allmand, 85, 255, 297, 300, 301, 305, 411.
 Andrews, 67.
 Appleby, 95.
 Arago, 207.
 Archibald, 62, 63.
 Arkadjev, 233.
 Arndt, 70, 399.
 Arrhenius, 24, 49, 53, 132, 137, 139, 143, 145, 155, 171, 340, 341.
 von Arsdale, 411.
 Ashcroft, 398.
 Askenasy, 407.
 Astachow, 256.
 Aten, 310, 394.
 Auerbach, 255.
 Auwers, 173.
 Ayrton, 230.
- B**ABOROVSKY, 108, 131.
 Bairsto, 310.
 Balbach, 391.
 Bancroft, 95, 173, 176, 247, 411.
 Banerji, 338.
 Barrett, 338.
 Barth, 173.
 Bates, 73, 78.
 Baur, 247, 255.
 Baxter, 157, 378.
 Beans, 255.
 Beattie, 207.
 Beck, 207.
 Becker, 338.
 Beckmann, 173.
 Becquerel, 251.
 Behr, 207.
 Bein, 131.
 Bell, 126.
- Bencowitz, 338.
 Bender, 157.
 Bennewitz, 274.
 Benrath, 70.
 Berthelot, 24, 151.
 Betts, 388.
 Billiter, 406, 408, 411.
 Billitzer, 272, 274.
 Biltz, 337.
 Bingham, 95.
 Bircher, 294.
 Bird, 404.
 Birkenstock, 131.
 Bishop, 57, 95.
 Bjerrum, 131, 199, 358, 378.
 Black, 157.
 Blake, 255, 272.
 Blüh, 364.
 Blumentritt, 366, 378.
 Bodforss, 272, 274.
 Bodlander, 247, 255.
 Böeseken, 95.
 Bogitch, 411.
 Bohi, 139.
 Boltzmann, 347.
 Born, 255.
 Bosch, 207, 255.
 Bouchet, 255.
 Bousfield, 90, 91, 93, 95.
 Bowden, 63, 292, 310.
 Boylston, 157.
 Braley, 256.
 Brann, 183, 207.
 Braune, 95.
 Bray, 59, 60, 64, 66, 72, 73, 82, 133, 378.
 Bredig, 51.
 Bretinger, 411.
 Brighton, 131, 197, 227.
 Brochet, 303.
 Brockman, 310.
 Brode, 397.
 Brodsky, 255, 378.
 Bronson, 230.
 Brönsted, 173, 310, 378.
 Brown, 304.
 Bruns, 129.
 Buchböck, 105, 131.
 Buckley, 200, 201, 221, 226, 250.
 Buff, 35.

Buhl, 255.
 Bülmann, 201.
 Bunting, 96.
 Busch, 80.
 Butler, 188, 191, 245, 269, 270, 274.
 Byers, 310.
 Byrne, 310.

CADY, 95, 255.
 Caplan, 290.
 Carnot, 2, 15, 17, 180, 184.
 Carrara, 255.
 Carroll, 68.
 Carter, 255.
 Carveth, 255.
 Caspari, 282.
 Castner, 396.
 Catteneo, 93.
 Cavanagh, 255.
 Centnerszwer, 60, 93, 149.
 Chang, 383.
 Chapman, 274, 338.
 Chappuis, 303.
 Chattaway, 181.
 Chaudhuri, 274.
 Chéneveau, 173, 255.
 Chow, 233, 255.
 Clack, 171.
 Clapeyron, 8.
 Clark, 230, 411.
 Clausius, 156, 345, 346.
 Cohen, 181.
 Colange, 274.
 Coleman, 53, 66.
 Collins, 35.
 Cooley, 411.
 Cormack, 328, 329, 338.
 Cottrell, 149, 310.
 Coulomb, 347, 359.
 Courtman, 96.
 Cowperthwaite, 96, 122, 358, 359.
 Craig, 256.
 Creighton, 131.
 Crenshaw, 234.
 Creutzfeldt, 411.
 Cumming, 216.
 Cuthbertson, 173.

D'AGOSTINI, 255.
 Dale, 156.
 Danner, 255.
 Darby, 63.
 Davies, 82, 95, 338.
 Davis, 173.
 Dean, 383.
 Debye, 8, 40, 53, 54, 78, 80, 126, 127, 339, 344, 354, 355, 356, 357, 358, 360, 361, 364, 365, 366, 369, 378.
 Delijannis, 274.

Denison, 115.
 Dieterici, 173.
 Diethelm, 247.
 Dietzel, 392.
 Dole, 104, 255.
 Donnan, 255.
 Drossbach, 255.
 Drücker, 131.
 Dubrisay, 274.
 Dulk, 310.
 Dunham, 256.
 Dunnill, 310.
 Duperthius, 80, 95.
 Dutoit, 95.

EASTMAN, 44.
 Eberlein, 255.
 Ebert, 95, 201, 358, 378.
 Eggert, 310.
 Einstein, 416.
 Eiseman, 290.
 Ekwall, 411.
 Ellingham, 288, 297, 300, 301, 411.
 Ellis, 199, 255.
 Elsas, 315, 338.
 Enos, 411.
 Essin, 411.
 Evans, 300, 310.
 Eversole, 234, 256.
 Evjen, 378.
 Ewart, 96.

FABIAN, 411.
 Fajans, 130, 159, 160, 253, 255, 358.
 Fales, 196.
 Falk, 41, 44, 46, 47, 51, 72, 86, 96, 105, 131.
 Falkenhagen, 369, 378.
 Faraday, 28, 97, 271, 393.
 Farr, 256.
 Fawsitt, 95.
 Fenwick, 228.
 Ferguson, A., 46, 47, 48, 51, 52, 74, 77, 78, 80, 360.
 Ferguson, A. L., 232, 255, 411.
 Féry, 255, 307.
 Fick, 166.
 Field, 411.
 Findlay, 102.
 Fink, 411.
 Finkelstein, 131.
 Fitzgerald, 95.
 Fleck, 337.
 Fleysher, 121, 378.
 Flugel, 173.
 Foerster, 247, 310.
 Fosbinder, 234, 255.
 France, 255.
 Franklin, 58, 59, 61, 63, 93, 95.
 Frary, 394.

Frazer, 24, 55, 80, 354.
 Fredenhagen, 378.
 French, 255.
 Frenkel, 131, 378.
 Freundlich, 272, 274.
 Frivold, 378.
 Frölich, 411.
 Frumkin, 269, 274.
 Fürth, 338.

GAGNAUX, 95.

Garrison, 252, 255, 272.
 Gauss, 413.
 Gerke, 207, 238, 240, 255.
 Gernet, 411.
 Getman, 131, 255.
 Ghosh, 274, 343.
 Gibbons, 131.
 Gibbs, 5, 21, 23, 24, 63, 176, 179, 267,
 269, 270, 308, 403.
 Gladstone, 156.
 Glaessner, 247.
 Glaser, 389.
 Glasstone, 27, 282, 293, 294, 296,
 310.
 Godlewski, 173.
 Goldmann, 252.
 Goldschmidt, 69, 95.
 Goode, 157.
 Goodwin, 272, 274, 338.
 Gorke, 95.
 Gorodetskaja, 274.
 Gouy, 269, 274.
 Grant, 222, 310.
 Green, 95.
 Grindley, 338.
 Gronwall, 378.
 Groshans, 164.
 Gross, 131, 378.
 Grotian, 38.
 Groves, 24.
 Grube, 247, 310, 411.
 Grünbaum, 236.
 Grüneisen, 95, 131.
 Guldberg, 24.
 Guthe, 35, 310.
 Gyemant, 378.

HAAS, 402.

Haber, 200.
 Hagenbach, 93.
 Hainsworth, 240, 255.
 Hale, 402, 409.
 Hall, 155.
 Halpern, 131, 378.
 Hammett, 255.
 Hammond, 411.
 Hantzsch, 173.
 Hargreaves, 404.
 Haring, 207, 255.

Harkins, 44, 283, 294, 304.
 Harned, 121, 233, 255, 357, 378.
 Hartley, 55, 79, 80, 95, 121, 125, 126,
 200, 201, 226, 250, 338, 354, 378.
 Harvey, 395.
 Haskell, 170, 338.
 Hausrath, 173.
 Haworth, 323, 334, 336.
 Heathcote, 310.
 Hedges, 310.
 Heidinger, 411.
 Heimrod, 35.
 Helfenstein, 35.
 Hellmann, 364.
 Helmholtz, 5, 181, 202, 271, 308,
 356.
 Henderson, 225, 236, 338.
 Herasymenko, 291, 310.
 Hermann, 247.
 den Hertog, 394.
 Herweg, 362.
 Herzfeld, 274.
 Herzog, 95.
 Hevesy, 107, 131, 310.
 Hey, 334.
 Heydweiller, 139, 164, 328.
 Heyrovský, 191, 255, 272, 291, 296.
 Hibbard, 338.
 Hibben, 131.
 Hicks, 149.
 Hiline, 411.
 Hirsch, 384.
 Hitchcock, 310.
 Hittorf, 28, 35, 45, 98, 301.
 Holborn, 35, 278, 311, 327, 338.
 Hollard, 338.
 Hopfgartner, 131.
 Hopfner, 392.
 Horsch, 207.
 Hotchkiss, 328, 338.
 Houlevigne, 35.
 Hückel, 40, 53, 54, 78, 80, 126, 127,
 130, 339, 344, 347, 354, 355, 357,
 358, 360, 361, 364, 365, 366, 378.
 Hughes, 255.
 Hulett, 234, 255.
 Hunt, 73, 135.

ISAACS, 237.

JAHN, 35, 127, 162, 173, 182, 232,
 233.
 Jaubert, 409.
 Johnston, 84.
 Jones, 68, 95, 104, 235, 255, 321.
 Joos, 159, 366.
 Josephs, 321.
 Joubert, 255.
 Jows, 95.

KAHLENBERG, 35, 64, 235, 255.

Kailan, 95.

Kameyama, 255.

Kandidow, 265.

Kandilof, 274.

Kane, 221.

Kanolt, 139.

Karpen, 255.

Kato, 131, 139.

Kawai, 134.

Kellner, 402.

Kendall, 50, 68, 95, 145, 154, 328, 329.

Kern, 388, 411.

Keyes, 66, 206, 207, 285.

Kieran, 68.

Kimreich, 275.

King, 95, 145, 325.

Kirchhoff, 7.

Kjellin, 255.

Kleeman, 175, 188, 274.

Klemeniewicz, 200.

Klemm, 337.

Knibbs, 298.

Knobel, 255, 284, 290, 293, 307.

Knowles, 409.

Knox, 329, 338.

Koch, 236, 255.

Kohlrausch, 28, 35, 38, 40, 45, 46, 47, 49, 70, 84, 90, 114, 118, 139, 278, 311, 326, 327, 328, 338, 339, 340, 343, 352, 353.

Kohlschutter, 411.

Korber, 95.

Krarup, 201.

Kraus, 47, 52, 57, 58, 59, 60, 64, 66, 67, 82, 85, 93, 95, 128, 144, 207, 237, 327, 332, 333.

Krouchkoll, 255, 265.

Krsnjač, 131.

Krüger, 270, 275.

Kunz, 94, 198, 247, 256.

Küster, 128.

LACEY, 207.

Laing, 69.

Lamb, 247.

La Mer, 378.

Lammert, 96.

Landolt, 162.

Langbein, 387.

Langdon, 310.

Langmuir, 299.

Larmor, 19.

Larson, 247, 378.

Laszczyński, 391.

Lattey, 82, 88, 296.

Le Blanc, 280, 303, 397.

Lehfeldt, 186.

Levier, 95.

Lewis, 6, 63, 116, 152, 197, 199, 206, 207, 226, 227, 254, 310, 370, 373, 374, 375, 376.

Leykam, 408.

Liebenoff, 308.

Liebreich, 271, 310, 389.

Limann, 173.

Lindemann, 109, 131.

Lindsay, 68.

Linhart, 207, 375, 376.

Lippmann, 265, 266, 271.

Lobry, 310.

Lodge, 113.

Loeb, 101, 131.

Loomis, 197, 199.

Lorentz, 156.

Lorenz, 74, 95, 107, 139, 156, 299, 393.

Lowenherz, 139.

Lowry, 90, 91, 93, 378.

Lucasse, 233, 378.

Lund, 201.

MACINNES, 96, 122, 131, 173, 212, 216, 217, 218, 226, 227, 240, 255, 294, 310, 358, 359, 377, 378.

Mackay, 121.

Magnanini, 68.

Maier, 411.

Mair, 155.

Malsch, 92.

Maltby, 93, 326, 327, 340.

Maneuvrier, 303.

Marchese, 391.

Marie, 338.

Marsh, 303, 304, 406.

Martin, 65, 66, 89, 95, 127.

Masson, 96, 114.

Mather, T., 230.

Mather, W. T., 131.

Mathers, 387, 388.

McAulay, 292.

McBain, 53, 63, 69, 128, 129, 358.

McDougall, 96.

McHenry, 255.

McIntosh, 62.

McKeown, 207.

McLewis, 236, 256.

McMaster, 95.

Meacham, 199.

Mercer, 310.

Merriam, 310.

Merritt, 335, 338.

Merton, 162.

Meyer, 255, 264.

Michaelis, 153.

Millard, 131.

Miller, 337.

Millikan, 85.

Milner, 53, 344, 355.

Moebius, 391.

Moore, 406.

Morgan, 96.
Morse, 24.
Mortimer, 255.
Moss, 204, 261, 313, 315, 322, 323.
Mudge, 195, 196.
Mueller, 157, 358.
Müller, 243, 255, 310, 378, 411.
Mullinix, 96.
Murdock, 252.
Mutzel, 131.

NAYDER, 364.

Neale, 173.
Nelson, 406.
Nernst, 1, 6, 70, 101, 131, 139, 141, 172, 185, 187, 204, 224, 288, 289, 310, 358, 360, 378.
Neuhausen, 234, 255.
Neustadt, 236, 255.
Newbery, 255, 285, 287, 295, 296, 316.
Newman, 303.
Nichol, 411.
Niederhauser, 255.
Nies, 130.
Nonhebel, 121, 378.
Noyes, 41, 44, 46, 51, 72, 78, 86, 96, 105, 131, 139, 141, 142, 143, 153, 183, 207, 256, 338, 378.

OKLEY, 65.

Obata, 182.
Oettel, 402.
Ogg, 250.
Ohm, 393.
Ohölm, 171, 172.
Onsager, 80, 81, 87, 128, 360, 361, 378.
Osaka, 173.
Osmond, 35.
Ostwald, 35, 50, 51, 134, 142, 161, 162, 176, 254, 340, 360.
Oudemans, 162.

PALMAER, 196, 203, 261.

Pan, 411.
Parker, 47, 52, 212, 216, 217, 218, 326, 327, 332, 333.
Partington, 95, 145, 237, 325, 341, 364.
Paschen, 262.
Paterno, 173.
Paterson, 411.
Patterson, 35.
Pearce, 149, 234, 255, 256, 336.
Peck, 128.
Pellat, 35.
Perrin, 273.
Peterson, 173.
Petit, 303.
Pfeiffer, 12, 329, 338.
Philip, 65, 96.

Pierce, 336.
Pike, 378.
Planck, 226.
Plotnikov, 96.
Poisson, 347, 349, 413, 420.
Popoff, 198, 247, 256.
Porter, 13, 177, 186, 361.
Potier, 35.
Potsch, 362.
Pound, 64, 68.
Prideaux, 229, 256.
Prscheborowsky, 64.
Puri, 305.

RAIKES, 95, 96, 125.

Ralston, 310.
Randall, 6, 152, 173, 197, 254, 370, 373, 374.
Randolph, 310.
Raoult, 24.
Rappeport, 95.
Rathert, 310.
Ratnowski, 362.
Rayleigh, 31, 35.
Read, 149, 326.
Redlich, 52.
Redman, 338.
Reed, 96.
Reichinstein, 310.
Reisener, 108, 109, 131.
Remy, 108, 109, 110, 112, 119, 131.
Reuss, 411.
Reychler, 128.
Reyher, 173.
Rhodin, 408.
Rice, 270.
Richards, 35, 155, 207, 256.
Richardson, 187.
Rideal, 188, 191, 294, 297, 310.
Riedel, 411.
Riesenfeld, 109.
Rimbach, 96.
Roberts, 228.
Robinson, 255.
Rodebush, 173.
Rokotjan, 96.
Rollet, 411.
Rona, 274.
Röntgen, 173.
Rosa, 35.
Rosenberg, 275.
Roshdestwensky, 236, 256.
Rothmund, 256, 264.
Rozsa, 173.
Ruby, 134.
Rudolphi, 71.
Rudorf, 84.
Ruer, 303.
Ruhoff, 64.
Rule, 364.
Rupert, 207.

Rutter, 247.
 Rysselberge, 129, 358.

SACH, 92.
 Sachanov, 64, 96.
 Sack, 363.
 Sackur, 13, 361.
 Sakhanov, 236.
 Sammet, 131.
 Sand, 275, 293.
 Sandved, 378.
 Sanigar, 411.
 Sargent, 226, 389.
 Sauer, 256.
 Scatchard, 127, 200, 216, 378.
 Schick, 303.
 Schiller, 378.
 Schischkin, 411.
 Schlecht, 411.
 Schlesinger, 66, 96, 326.
 Schlotter, 390.
 Schmick, 96, 131.
 Schmidt, 96, 310.
 Schneider, 173, 256.
 Schoch, 310, 384, 411.
 Schofield, 269, 271.
 Scholl, 252.
 Schreber, 173, 256.
 Schreiner, 129, 161, 378.
 Schuckert, 409.
 Schulze, 302, 310.
 Scott, 173.
 Sebastian, 197, 228.
 Seith, 275.
 Sen, 274.
 Senter, 310.
 Seward, 144.
 Shaw, 35, 230.
 Sheppard, 253.
 Sherrill, 378.
 Shields, 138.
 Shinn, 64.
 Sidgwick, 35.
 Siemens, 390, 406.
 Simonds, 274.
 Skinner, 35.
 Slade, 310.
 Smith, E. R., 122, 131.
 Smith, F. A., 326, 338.
 Smith, F. E., 31, 230.
 Smith, S. W. J., 98, 204, 259, 261, 275, 313, 315, 322, 323.
 Smits, 173, 175, 302, 310, 382.
 Smoluckowski, 256, 272.
 Snow, 198, 256.
 Solvay, 407.
 Soret, 24.
 Sosman, 139, 272, 274.
 Spitzer, 310, 383, 411.
 Spooner, 256.
 Stapenhorst, 310.

Stearn, 135.
 Steele, 62, 115, 116.
 Stegeman, 275.
 Steinour, 256.
 Stern, 13, 275.
 Stiles, 172.
 Stokes, 36, 85, 120, 125, 126, 357, 420.
 Störbeck, 247.
 Storch, 71, 76, 207.
 Streintz, 309.
 Stroud, 338.
 Stscherbakow, 411.
 Sturdevant, 411.
 Sugden, 131.
 Sutherland, 342.
 Svedberg, 256, 272.
 Symes, 310.
 Szyszkowski, 83.

TAKEUCHI, 275.
 Talmund, 275.
 Taniakivsky, 291.
 Tartar, 285.
 Taussig, 407.
 Taylor, 63, 256, 320, 322, 335, 398.
 Thomas, 95.
 Thomsen, 151, 152, 154, 179, 309.
 Thomson, 5, 35.
 Thönnessen, 129.
 Thuesen, 95.
 Thum, 391.
 Tibballs, 128.
 Titley, 69.
 Toabe, 207.
 Tollinger, 315.
 Tolman, 232.
 Tombrock, 181.
 Townsend, 404.
 Traube, 164.
 Tretjakov, 378.
 Trivelli, 253.
 Tucker, 252.

ULICH, 80, 87, 96, 107, 109, 121, 364.
 Ulrey, 175.

VALSON, 163, 165.
 Vanselow, 173, 253.
 Van der Waals, 24.
 van't Hoff, 13, 18, 42, 71, 140, 146, 150, 151.
 Veazey, 95.
 Veibel, 256.
 Vinal, 35.
 Vogel, 46, 47, 48, 51, 52, 74, 77, 78, 80, 360.
 von Halban, 95.
 Vosburgh, 195, 256.

W

AAGE, 24.

Wagner, 108, 131.

Wainoff, 70.

Walden, 60, 64, 78, 86, 93, 96, 120, 149,
173, 363, 364.

Walker, 328, 338.

Wallace, 337.

Walpole, 228.

Walter, 310.

Warburg, 335.

Wasastjerna, 96, 159.

Washburn, 52, 74, 84, 96, 105, 110, 131,
149, 212, 326, 338, 340.

Watkins, 95.

Watts, 310, 411.

Weber, 114.

Weeks, 293.

Wegscheider, 51.

Weiland, 52, 340.

Weitzel, 96.

Werner, 364.

Wessel, 109, 131.

Westenberg, 394.

Weston, 230.

Westrip, 293.

Wheeler, 63.

Whetham, 35, 96, 113, 125, 129, 173,
333.

Whiting, 408.

Whitney, 255.

Wiedemann, 83, 173.

Wiederholt, 310.

Wien, 92, 338, 365, 378.

Wijs, 138, 139.

Wild, 265, 275.

Wildermann, 252, 408.

Wilke, 378.

Williams, 369, 378.

Winninghoff, 66.

Winther, 256.

Wolf, 84.

Wolfenden, 221.

Wolff, 335.

Wörmann, 153.

Wosnessensky, 256.

Wreschner, 274.

Wright, 221.

Y

AMASAKI, 247.

Yeh, 227, 255.

Yorke, 96.

Z

AHN, 364.

Zwicky, 378.

SUBJECT INDEX.

(The numbers refer to pages.)

- A**BSOLUTE electric charge on ions, 33.
 — ionic velocities, 123.
 — transference numbers, 107, 109.
 — zero of potential, 197, 271.
 Accumulators, 178, 183, 306.
 Acetaldehyde, conductance of salts in, 64.
 Acetic acid, equilibrium constant, 50.
 Acetone, conductance of salts in, 64, 79, 130, 236.
 Acker process, 409.
 Action, secondary, electrolytic, 27, 383.
 Activity, 370.
 — and E.M.F. measurements, 371.
 — — freezing-point temperatures, 375.
 — — mass law, 374.
 — coefficients, 372.
 — — of individual ions, 376.
 — mean, 376.
 Addition agents, 386.
 Additive properties of electrolytes, 134, 156, 157, 161, 163.
 Adiabatic changes, 2.
 Adsorption, 24, 205, 269.
 — Gibbs' equation for, 21, 267.
 Affinity, electron, 187, 191.
 Alcohols, conductivity of salts in, 54, 65, 69, 79, 89, 93, 121, 125, 127, 129, 130, 236, 237.
 Allen-Moore cell, 406.
 Alloys, 383.
 Alternating current electrolysis, 303.
 — — used in measuring conductance, 315.
 Aluminium, refining of, 394.
 — refraction of ion, 159.
 Amalgams in capillary electrometers, 265.
 — — concentration cells, 234.
 Ammonia, conductance of alkali metals in, 66.
 — — — electrolytes in, 58.
 — equilibrium constant, 60.
 — ionic mobilities in, 60.
 Ampere, definition of, 30.
 Amylamine, conductance of electrolytes in, 64.
 Aniline, conductance of electrolytes in, 64.
 Anions, definition of, 26.
 Anode, definition of, 25.
 — effect, 398.
 Anodic overvoltage, 289.
 — — theories of, 299.
 Anolyte, definition of, 392.
 Available energy, *see* Free energy.
- B**ACK E.M.F., 277, 313.
 Balbach-Thum process, 391.
 Bath, electrolysis, 384.
 Benzonitrile, conductance of salts in, 65.
 Billiter-Leykam cell, 408.
 — -Siemens cell, 406.
 Binary electrolytes, definition of, 28.
 Bipolar electrodes, 384.
 Boiling-point temperature of a solution, 15, 149.
 Boltzmann's principle, 347.
 Boric acid solutions, conductance of, 68.
 Brine, electrolysis of, 400.
 Bromates, electrolytic preparation of, 410.
 Bromine, electrolytic preparation of, 410.
 Brownian motion, 360, 415.
 Buffering agents, 382.
- C**ADMIUM cell, 230.
 Calcium, production of, 398.
 Calomel electrodes, 194.
 Capacity of electrolytic cell, 279, 312, 333, 334.
 — specific inductive, *see* Dielectric constant.
 Capillary effects, *see* Electro-capillarity.
 — electrometers, 257, 272.
 Carnot-Clausius equation, 3.
 — cycle, 2, 181.
 Castner process, 396.

- Cataphoresis, 274.
 Caustic alkali, preparation of, 405.
 Cells, alkali-chlorine, 403.
 — cadmium, 230.
 — changes produced by current in, 98.
 — chlorate, 403.
 — Clark, 230.
 — concentration, 178, 210.
 — — amalgam, 234.
 — — applications of, 247, 377.
 — — calculation of E.M.F. of, 212, 371.
 — — containing mixed electrolytes, 233, 235.
 — — measurement of E.M.F. of, 222.
 — — temperature coefficient of, 182, 238.
 — — thermodynamics of, 212.
 — — with transference, 210, 212, 215.
 — — — E.M.F. of, 217, 232.
 — — without transference, 211, 213, 218.
 — — — E.M.F. of, 219, 232, 238.
 — conductivity, 325.
 — diaphragm, 404.
 — gas, 238, 242.
 — gravity, 408.
 — half, 194, 198.
 — mercury, 406.
 — oxidation-reduction, 178, 240.
 — photo-voltaic, 251.
 — reversible and irreversible, 177, 251.
 — standard, 230.
 — voltaic, 174.
 — — E.M.F. of, 179, 192.
 Chlorate cells, 403.
 — production of, 400, 403.
 Chlorine, production of, 403.
 Chrome yellow, production of, 409.
 Chromium-plating, 389.
 Clapeyron's equation, 8.
 Coefficient of diffusion, 166.
 Colour of salt solutions, 161.
 Commutator method for overvoltage measurements, 282, 284.
 Complete ionisation, theory of, *see* Dissociation.
 Complex ions, 27, 44, 95, 103, 127, 135, 194, 233, 237, 358.
 Components, definition of, 11.
 Compounds, electrolytic, preparation of, 410.
 Concentrated solutions, equation for, 13.
 Concentration cells, *see* Cells, concentration.
 — curves, *see* Curves.
 — influence of, on conductance, 70.
 — polarisation, 276.
 Conductance cells, 325.
 — definition of, 38.
 — dispersion, 368.
 Conductance equivalent, determination of, at infinite dilution, 72, 87.
 — — formula for, 38, 71, 74, 78, 80, 82, 87, 339, 343, 353, 361.
 — — values of, 41, 75, 137.
 — influence of applied E.M.F. on, 365.
 — — — concentration, 39, 55, 70, 343, 347, 357, 360, *see also* Equivalent conductance.
 — — — fluidity, 83.
 — — — impurities, 40, 68, 331.
 — — — temperature, 62, 89.
 — — — viscosity, 83.
 — measurement of, 311.
 — of alkali metals in ammonia, 66.
 — — electrolytes in acetone, 64, 79, 130, 236.
 — — — alcohols, 54, 65, 69, 79, 89, 93, 121, 125, 127, 129, 130, 236, 237.
 — — — ammonia (liquid), 58, 93, 237.
 — — — aniline, 64, 236.
 — — — benzonitrile, 65, 89, 127.
 — — — hydrochloric acid, 63.
 — — — hydrogen bromide (liquid), 62.
 — — — iodine, 63.
 — — — mixed solvents, 67, 130.
 — — — nitromethane, 65.
 — — — pyridine, 64, 80, 235, 236.
 — — — sulphur dioxide (liquid), 60, 93.
 — — — various solvents, 63, 80, 93, 126.
 — — fused electrolytes, 70, 337, 393.
 — — ions, *see* Ions, mobility.
 — — mixed electrolytes, 93, 134.
 — — non-aqueous solutions, 54, 93.
 — — soap solutions, 69.
 — — water, 137, 327.
 — — — correction for, 329.
 — — weak solutions, 331.
 — specific, formula for, 37, 134.
 — — of water, 137, 327.
 — — — standard solutions, 327.
 — — temperature coefficient of, 90.
 Conduction process, 36, 97.
 Conductivity, *see* Conductance.
 — water, 328.
 Constant, equilibrium, *see* Equilibrium constant.
 Co-ordinates, generalised, 4, 8.
 Copper electro-plating, 390.
 — — refining, 391.
 Cuprous oxide, preparation of, 410.
 Current, alternating, used in measuring resistance, 315.
 — diffusion, 291.

- Current efficiency, 380, 407.
 — leakage, 314.
 Curves, conductance and E.M.F., 367.
 — — — temperature, 93.
 — — — dispersion, 370.
 — electro-capillary, 261.
 — equivalent conductance and concentration, 38, 39, 82.
 — — — — viscosity, 89.
 — — — effect of impurities, 332.
 — — — of KI in solvents, 79.
 — graphical method for the determination of value of Λ_0 , 73.
 — hydrogen overvoltage, 292.
 — mobility of ions in solvents, 57.
 — molecular refraction and concentration, 160.
 — Storch's dilution equation, 76.
 Cyanoacetic acid, equilibrium constant of, 59.
 Cycle, Carnot, 2, 15, 17, 180, 184.
 — irreversible, 3.

- D**EBYE and Hückel's theory of strong electrolytes, 54, 347.
 Decomposition voltage, 279.
 Degree of ionisation, 41, 51, 70, 122, 132, 146, 149, 163, 217.
 Deposition potential, 28, 379, 382.
 Depression, molecular, *see* Molecular depression.
 — freezing-point, *see* Freezing-point depression.
 Dielectric constant, 25, 78, 81, 235, 346, 349, 357, 361.
 — — variation of, 362.
 Dietzel cell, 392.
 Diffusion, 166.
 — coefficients, 166.
 — — of electrolytes, 171.
 — — temperature coefficient of, 172.
 — currents, 291.
 — potentials, 229.
 Dilution law, Ostwald's, 50, 340.
 Dipoles, 106.
 Dispersion, conductance, 368.
 Dissociation, electrolytic, degree of, 41, 43, 51, 58, 70, 82, 86, 89, 94, 122, 123, 125, 132, 146, 149, 163, 217, 340, 358, 373.
 — — theory of, 31, 53, 78, 147, 342, 357.
 — — variation of, with concentration, 39, 52, 69, 71, 128, *see also* Degree of electrolytic dissociation.
 — heat of, 21, 150.
 — of water, 137.
 Doublets, 106.
 Dropping electrodes, 202, 261, 270.

- E**FFICIENCY of Carnot cycle, 2.
 — — current in electrolysis, 380, 409.
 Electrical charge on ions, 26.
 — double layer, 174, 257.
 — force of relaxation, 367.
 Electro-affinity, 186.
 Electro-capillarity, 257.
 — theories of, 265.
 Electro-capillary adsorption of ions, 269.
 — curves, 259, 267, 270.
 — measurements, 262.
 — phenomena at interfaces, 264.
 Electro-chemical equivalents, 29, 33, 34.
 Electro-endosmosis, 273.
 Electro-kinetic phenomena, 273.
 Electrode potential, 184, 205, 207, 208, 209, 382.
 — — theories of, 187.
 — — reactions, 254.
 Electrodes, calomel, 194, 272.
 — dropping, 202, 261, 270.
 — glass, 200.
 — hydrogen, 196, 246, 248.
 — quinhydrone, 201.
 — silver chloride, 200, 240.
 — standard, 194, 200.
 Electrolysis, 25.
 — alternating current, 303.
 — bath, 384.
 — concentration changes produced by, 98.
 — Faraday's law of, 28, 97.
 — of brine, 400.
 — — fused electrolytes, 393.
 — technical applications of, 379.
 Electrolytes, 25.
 — additive properties of, 163.
 — bi-bivalent, 28.
 — binary, 28.
 — capillary-active and inactive, 263, 269.
 — conductance of, 25, *see also* Conductance.
 — — — and depression of freezing-point, 42, 149.
 — — — — elevation of boiling-point, 149.
 — diffusion of, 166.
 — fused, conductance of, 70, 337, 393.
 — intermediate, 40.
 — ionisation of, *see* Dissociation.
 — law of mass action applied to, 49.
 — mixed, equilibria of, 132, 134, 233.
 — solubility of, 139.
 — strong, 40, 51, 53.
 — — theories of, 341.
 — tertiary, 28.
 — thermal properties of, 150.
 — uni-univalent, 28, 81.

- Electrolytes, weak, 40.
 Electrolytic cell, capacity of, 279, 312, 334.
 — conduction process, 36.
 — deposition, 379.
 — preparation of compounds, 410.
 — processes, 409.
 — resistance, 311, 322.
 — solutions, definition of, 25.
 — — diffusion in, 166.
 — — optical properties of, 156.
 — — temperature coefficients of, 90.
 — — theories of, 339.
 — transference of water, 110.
 Electrometers, capillary, 257, 272.
 Electrometric titrations, 249.
 Electromotive force, 174.
 — — and temperature, 199.
 — — — transference numbers, 232.
 — — back, 277, 311, 313.
 — — of concentration cells, 212, 222, 371.
 — — — dropping electrodes, 204, 262, 264.
 — — — gas cell, 278.
 — — — hydrogen-calomel cells, 200, 201.
 — — — standard half-cells, 195, 196, 197, 200, 201.
 — — — voltaic cell, 179.
 — — variation of, with concentration, 192.
 — series, 208.
 Electron affinity, 187, 191.
 Electro-plating, 379, 385.
 — by brass, 390.
 — — chromium, 389.
 — — copper, 390.
 — — gold, 389.
 — — iron, 390.
 — — lead, 388.
 — — silver, 389.
 — — tin, 387.
 — — zinc, 388.
 Electro-refining, 379, 391.
 — of copper, 391.
 — — gold, 392.
 — — nickel, 392.
 — — silver, 391.
 — — tin, 393.
 — — zinc, 393.
 Elevation, molecular, of boiling-point, 16, 149.
 Endosmosis, 273.
 Energy, free, 4, 9, 19.
 — — and electro-capillary effects, 22, 268.
 — — — electromotive force, 179, 308.
 — — — heat of ionisation, 254.
 — — — — solution, 150.
 — — — oxidation-reduction processes, 243.
 Energy, internal, 1.
 — — interfacial, 20, 257, 263, 266.
 Engine, thermodynamic, 212.
 Entropy, 3.
 Equation of adsorption, 21.
 — — Clapeyron, 8.
 — — Gibbs-Helmholtz, 5.
 — — isochore of reaction, 21.
 Equilibrium of systems, 9, 132, 150.
 — conditions of, 9.
 — constant, 19.
 — electrolytic, 50, 132, 243, 249, 329, 340.
 — — constant of, 50, 59, 60, 71, 74, 77, 132, 138, 142, 150.
 — — — water, 138, 249, 330.
 — — — and activity, 379.
 — — — solubility, 142, 150.
 — — — temperature, 20, 155.
 Equivalent conductance at infinite dilution, 38, 72, 87.
 — — effect of impurities on, 40, 68.
 — — influence of concentration on, 38, 71, 74, 78, 80, 82, 87, 339, 343, 353, 361.
 — — of electrolytes in acetone, 64, 79.
 — — — — alcohols, 55, 79, 81.
 — — — — liquid ammonia, 59.
 — — — — sulphur dioxide, 61.
 — — — — pyridine, 64.
 — — — — water, 39, 41, 75, 79, 82, 87, 89, 137.
 — — — ions, 45, *see also* Mobility of ions.
 — electro-chemical, 29, 33, 34.
 Ether solutions, conductance of, 68.
 Ethyl alcohol, conductance of salts in, 69, 79.
 Ethylamine, conductance of salts in, 64.
FARADAY, the, definition of, 33.
 Faraday's law of electrolysis, 28, 97, 271.
 Fick's law of diffusion, 166.
 First law of thermodynamics, 1.
 Flowing junctions between electrolytes, 227.
 Fluidity and relation with conductance, 83.
 Forces, generalised, 4, 8.
 Formic acid, conductance of salts in, 65.
 Free energy, *see* Energy.
 Freezing-points, depression of, 17, 146, 347.
 — — — and activity, 375.
 — — — relation with conductance, 42, 147, 149.
 Fugacity, definition of, 370.

Fused electrolytes, conductance of, 70,
337.
— — electrolysis of, 393.

GAS cells, 238, 242.
Gauss's theorem, 413.
Generalised co-ordinates, 4, 8.
— forces, 4, 8.
Gibbs' adsorption equation, 21, 267.
Gibbs-Helmholtz equation, 5.
Glass electrode, 200.
Gold electro-plating, 389.
— — refining, 392.
Gram-atom, definition of, 34.
Gram-equivalent, definition of, 35.
Graphical method of determining value
of Λ_0 , 73.

HAAS-OETTEL cell, 402.
Half-cells, 194, 200.
Hargreaves-Bird cell, 404.
Heat absorbed, sign of, 1.
— content, ionic, 253.
— — total, 6.
— latent, 8, 16, 17, 18.
— of dissociation, 21, 150, 154, 254.
— — — of water, 152.
— — ionisation, *see* Heat of dissociation.
— — neutralisation, 153.
— — reaction, 179, 238, 243.
— — solution, 150, 151.
— reversible effect in cells, 182, 254.
— theorem, Nernst, 6.
Homogeneous ionic equilibria, 132.
Hopfner process, 392.
Hydration of ions, 40, 94, 107, 108.
Hydrion, 26.
Hydrochloric acid, dissociation of, 359.
— — conductance of salts in, 63.
Hydrogen bromide solutions, conductance of, 62.
— cell, 239.
— electrodes, 196, 240, 246, 248.
— electrolytic production of, 409.
— overvoltage, 281, 290.
— — theories of, 296.
— scale of potential, 205.
Hydrolysis, 139.
Hypochlorites, production of, 401.

IMPURITIES, effect of, on conductance, 40.
Independent migration of ions, 45, 56, 164.
Individual ionic heat contents, 253.
Inter-ionic electrical forces, 53, 78, 147, 342, 360, 364.
Intermediate electrolytes, 40.

Internal energy, 1.
Inversion rate, 53.
Iodine, conductance of salts in, 63.
Ion, equation of motion of, 415.
Ionic atmosphere, 348.
— equilibria, 132.
— heat contents, 253.
— micelle, 69.
— mobility, 45, 46, 48, 56, 60, 70, 84, 88, 91, 112, 120, 121.
— — true, 112.
— strength, definition of, 374.
Ionisation, *see* Dissociation.
Ions, 26, 31.
— absolute velocity of, 37, 98, 112, 123, 124, 169, 229.
— additive properties of, 157, 161, 163.
— capillary-active and inactive, 263.
— complex, 27, 44, 95, 103, 127, 136, 194, 233, 237, 358.
— dimensions of, 106, 125, 357, 358.
— equivalent conductance of, *see* Ionic mobility.
— hydration of, 40, 94, 107, 108.
— migration of, 45, 97.
— — independent, 45, 156, 164.
— solvation of, 105, 125.
— specific refraction of, 159.
Irreversible cycle, 3.
— cells, 250.
Isoamyl alcohol, conductance of salts in, 65.
Isochores of reaction, 21.
Isohydric solutions, 132, 135.
Isothermal changes, 2.

JAUBERT cell, 409.

KATHODE, 25.
Kathodic overvoltage, 286, 287, 293, 294.
— — theories of, 296.
Katholyte, 392.
Kations, 26.
Kellner cell, 402.
Knowles cell, 409.
Kohlrausch bridge, 319, 320.

LATENT heat and boiling-point, 8, 16.
— — — freezing-point, 8, 17.
— — — molecular depression, 18.
— — Clapeyron's equation, 8.
Laszczyński process, 391.
Law, Faraday's, of electrolysis, 28.
— Fick's, of diffusion, 166.
— Gibbs', of adsorption, 21.
— Kohlrausch's, of independent ionic migration, 45.

Law of free energy, 5.
 — — mass action, 18.
 — — — — applied to electrolytes, 49, 374.
 — Ostwald's, of dilution of electrolytes, 50, 340.
 — Stokes', 71.
 — Walden's, of mobility and viscosity, 86.
 Laws of equilibrium of systems, 9.
 — — osmotic pressure, 12.
 — — thermodynamics, 1, 2.
 Lead, electrolytic production of, 409.
 — electro-plating, 388.
 — peroxide, 410.
 Leakage current, 314.
 Liquid-liquid potentials, 168, 215, 223, 229, 260.

MMAGNESIUM, production of, 395.
 Magnetic rotation of solutions, 162.
 Marchese process, 391.
 Marsh cell, 406.
 Mass action, law of, 18, 50, 52, 59, 65, 374.
 Mean activity of ions, 376.
 Membranes, diffusion potential at, 229.
 Mercury cells, 406.
 — dropping electrodes, 202, 261, 270.
 Metal-solution interface, potential difference at, 184.
 Methyl alcohol, conductance of salts in, 54, 68, 79, 81.
 — — ionic mobilities in, 56.
 Methylamine, conductance of solutions, 63.
 Migration of ions, 45, 56, 97.
 Milner's theory of strong electrolytes, 344.
 Mixed electrolytes, conductance of, 134.
 — — equilibria of, 132.
 Mobility of ions, 45, 46, 48, 56, 60, 70, 84, 88, 91, 112, 120, 121.
 — — — relation with temperature, 48, 84.
 — — — — viscosity, 83.
 — — — true, 112.
 Moduli, 165.
 Moebius process, 391.
 Mole, definition of, 12.
 Molecular depression, 17, 147, 347.
 — elevation, 16, 149.
 — refraction, 158, 160.
 — weight, 17, 44.
 Moving boundary method for transference numbers, 112.

NELSON cell, 406.
 Nernst heat theorem, 6.

Neutralisation, heat of, 153.
 — point, 249.
 Nickel refining, 392.
 Nitromethane, conductance of salts in, 65.
 Non-aqueous solutions, conductance of, 54.
 — — mass law of, 65.
 — solvents, solubility in, 144.
 Normal oxidation-reduction potential, 244.
 — electrode potentials, 205.
 Null-solutions, 204, 260.

OHM'S law in electrolytes, 31, 393.
 Onsager's theory of strong electrolytes, 80, 360.
 Optical properties of electrolytic solutions, 156.
 Orientation of solvent molecules, 106, 362.
 Osmotic phenomena, 12, 18, 146.
 — pressure, 12, 167, 174, 184.
 — — laws of, 12.
 — — of concentrated solutions, 13.
 — — relation with vapour pressure, 13.
 Ostwald's dilution law, 50, 134, 142, 340.
 Overpotential, *see* Overvoltage.
 Overvoltage, 281.
 — anodic, 289.
 — cathodic, 287.
 — measurement of, 282.
 — theories of, 296.
 — variation of, 292.
 Oxidation-reduction cells, 178, 240.
 — potentials, 243.
 — processes, 241.
 Oxygen, electrolytic production of, 409.
 — overvoltage, 289, 299.

PASSIVITY, 303.
 pH, 248, 382.
 Phase rule, 11.
 Phases, equilibrium of, 267.
 Photo-voltaic cells, 251.
 Platinode electrolyser, 402.
 Poisson's equation, 347, 349, 413, 420.
 Polarisation, 251, 276, 298, 311, 315.
 — capacity of electrolytic cell, 279, 312, 333.
 — measurement of, 277.
 Polar molecules, 362.
 Potassium chloride, equilibrium constant of, 52.
 Potential, *see also* Electromotive force.
 — absolute zero of, 197, 271.
 — deposition, 28, 379, 382.

Potential difference at mercury-solution interface, 202, 257.
 — — — metal-solution interface, 174, 184, 192, 202, 262, 266.
 — diffusion, 229.
 — electrode, 174, 184.
 — — theories of, 187.
 — liquid-liquid, 168, 215, 223, 229, 260.
 — normal electrode, 205.
 — of half-cells, 196, 197, 199, 200, 201.
 — oxidation-reduction, 243.
 — scales of, 205.
 — sign of, 176.
 — thermodynamic, 4, 9, 23, 268.
 Pressure, effect of, on E.M.F. of hydrogen cell, 239, 240.
 — — — — overvoltage, 294.
 — osmotic, *see* Osmotic pressure.
 — solution, 174, 186, 192, 204, 214.
 Principles, thermodynamic, 1.
 Process, reversible, 2.
 Propyl alcohol, conductance of salts in, 57, 65.
 Pyridine, conduction of salts in, 64.

QUINHYDRONE electrode 201.
 — Quino-quinhydrone electrode, 201.

REACTION, heat of, 179, 238, 243.
 — isochores of, 21.
 Reduction, normal, potential, 244.
 — processes, 241.
 Reduction-oxidation cells, 240.
 Refraction, molecular, 158, 160.
 — specific, 157, 159.
 Refractive index of solutions, 156.
 Refractivity, specific, 156.
 Relaxation, force of, 367.
 — time of, 367.
 Resistance, electrolytic, effective, 312.
 — — experimental results, 322, 337.
 — — measurement of, 311.
 — — variation of, 322.
 — transfer, 286, 295.
 Reversible cells, 177, 179.
 — cycles, 2, 15, 17.
 Rhodin cell, 408.
 Rotation, magnetic, of solutions, 162.
 Rule, phase, 11.

SALICYLIC acid, conductance of, 63, 68.
 — — solubility of, 145.
 Salting-out process, 106.
 Salts, solubility of, 139.
 — — — in presence of other salts, 143, 144.
 Scales of potential, 205.

Schuckert cell, 409.
 Second law of thermodynamics, 2.
 Secondary action, 27, 383.
 Series, electromotive, 208.
 Silver bromate, solubility of, 142.
 Silver-chloride electrode, 200, 240.
 Silver electro-plating, 389.
 — — refining, 391.
 Single potential differences, *see* Electrode potential.
 Soap solutions, conductance of, 63, 69.
 Sodium chloride, equilibrium constant of, 52.
 — metallic, production of, 396.
 Solubility of electrolytes, 139, 249.
 — — — in non-aqueous solvents, 144, 236.
 — — — — presence of other electrolytes, 141.
 — — — mutual influence on, 141.
 — — — relation with heat of solution, 150.
 — product of electrolytes, 140, 250.
 Solution, boiling-point temperature of, 15, 149.
 — freezing-point temperature of, 17, 146.
 — heat of, 150, 151.
 — pressure, 174, 186, 192, 204, 212.
 — vapour pressure of, 13.
 Solutions, isohydric, 132, 135.
 — specific inductive capacity of, *see* Dielectric constant.
 — weak, conductance of, 331.
 Solvation of ions, 105, 125.
 Solvay-Kellner cell, 407.
 Solvent, transport of, 107.
 Solvents, mixed, conductance of salts in, 67.
 Specific conductance, *see* Conductance.
 — inductive capacity, *see* Dielectric constant.
 — refraction, 157, 159.
 — refractivity, 156.
 Standard half-cells, or electrodes, 194, 198.
 Stokes's law, 36, 85, 120, 125, 126, 357, 420.
 Strong electrolytes, 40, 51, 53, 134.
 — — anomaly of, 341.
 — — theories of, 339-61, 370-8.
 Sulphur dioxide, conductance of salts in liquid, 60, 150.
 Sulphuric acid, dissociation of, 26.
 Surface, or interfacial, tension, 21, 257, 263, 266.
 Systems, equilibrium of, 9.
 — non-variant, 11.

T ABLES—
 Activity coefficients, 373, 374.
 Decomposition voltage, 280.

Tables (*cont.*)—

Degree of ionisation of electrolytes, 43.
 Diffusion coefficients, 171, 172, 173.
 Electro-capillary measurements, 262.
 — -chemical equivalents, 34.
 Electromotive force of cells, 217, 218, 219, 220, 232, 234, 236.
 Equilibrium constants, 51, 60, 77.
 Equivalent conductance of solutions, 41, 55, 57, 60, 61, 64, 65, 67, 69, 75, 81, 137, 354.
 — — relation with viscosity, 88.
 Heat of dissociation of water, 153.
 — — neutralisation, 155.
 — — reaction, 182.
 — — solution, 151.
 Hydration numbers, 108.
 Independent migration of ions, 46.
 Ionic product of water, 139.
 — velocities, 124.
 Mobilities, or ionic conductances, 48, 56, 60, 122, 123.
 Mobility, related with viscosity, 88.
 Moduli of ions, 166.
 Molecular conductance, 62.
 — depressions, 148.
 Overvoltages, 286, 290, 291.
 Oxidation potentials, 246, 247.
 Potential of electrodes, 199, 200, 207.
 — — liquid-liquid junctions, 225, 227, 229.
 Radii of ions, 126, 127.
 Refraction of electrolytes, 158, 161.
 Relaxation effects, 369.
 Solubility and solubility products, 142, 143, 144, 145, 250.
 Solvation numbers, 107.
 Specific conductance of fused salts, 70.
 — — — mixed electrolytes, 136.
 Temperature coefficients, 49, 90.
 Transference numbers, 104, 111, 119, 120.
 van't Hoff's factor, 150.
 Technical cells, 402.
 Temperature, boiling-point, of solution, 15, 149.
 — coefficients, of cells, 238.
 — — — ionic mobility, 49.
 — — — solutions, 90.
 — conductance relations, 89.
 — freezing-point, of solution, 17, 146.
 Tertiary electrolytes, 28.
 Theorem of Gibbs, 23.
 Theory of electrolytes, 31, 49, 339, 370.
 Thermal properties of electrolytes, 150.
 Thermodynamic potential, 4, 9, 23, *see also* Free energy.
 — principles, 1.
 Thermodynamics, laws of, 1, 2.
 Tin, electro-plating, 387.

Titration, electrometric, 249.
 Total heat content, 6.
 Townsend cell, 404.
 Transfer resistance, 286, 295.
 Transference numbers, 45, 56, 100, 211, 226, 377.
 — — by Hittorf's method, 100.
 — — — moving boundary method, 112.
 — — from E.M.F. measurements, 232, 237.
 — — importance of, 122.
 — — in mixed solutions, 121.
 — — — non-aqueous solvents, 120.
 — — relation with concentration and temperature, 103.
 — — true, 107, 109.
 — — values of, 104, 109, 119, 232, 237.
 Triple point, 11.
 True mobilities, 112.

VALENCY, determination of, from E.M.F. measurements, 250.
 — factors, 78.

Valve action, 302.
 van't Hoff's factor, 42, 146, 149, 375.
 Vapour pressure of solution, 13.
 Velocity of ions, 112, 123, 229.
 Virial, 345, 356.
 Viscosity, coefficient of, 42, 91.
 — correction in conductance measurements, 86.
 — relation with conductance, 83, 89.
 Voltage, decomposition, 279.
 Voltaic cells, *see* Cells.
 — elements, 176, 193.
 Voltameters, 29.

WALDEN'S rule for mobility and viscosity, 86, 120.

Water, conductance of, 327.
 — — — correction for, 329.
 — conductivity, preparation of, 328.
 — dissociation of, 137.
 — heat of dissociation of, 152.
 — specific conductance of, 329.
 — transference of, 110.
 Weak electrolytes, 40.
 Weights, molecular, determination of, 17.
 Weston cell, 230.
 Whiting cell, 408.
 Wien effect, 365.
 Wildermann cell, 408.
 Work, expression for, 2.

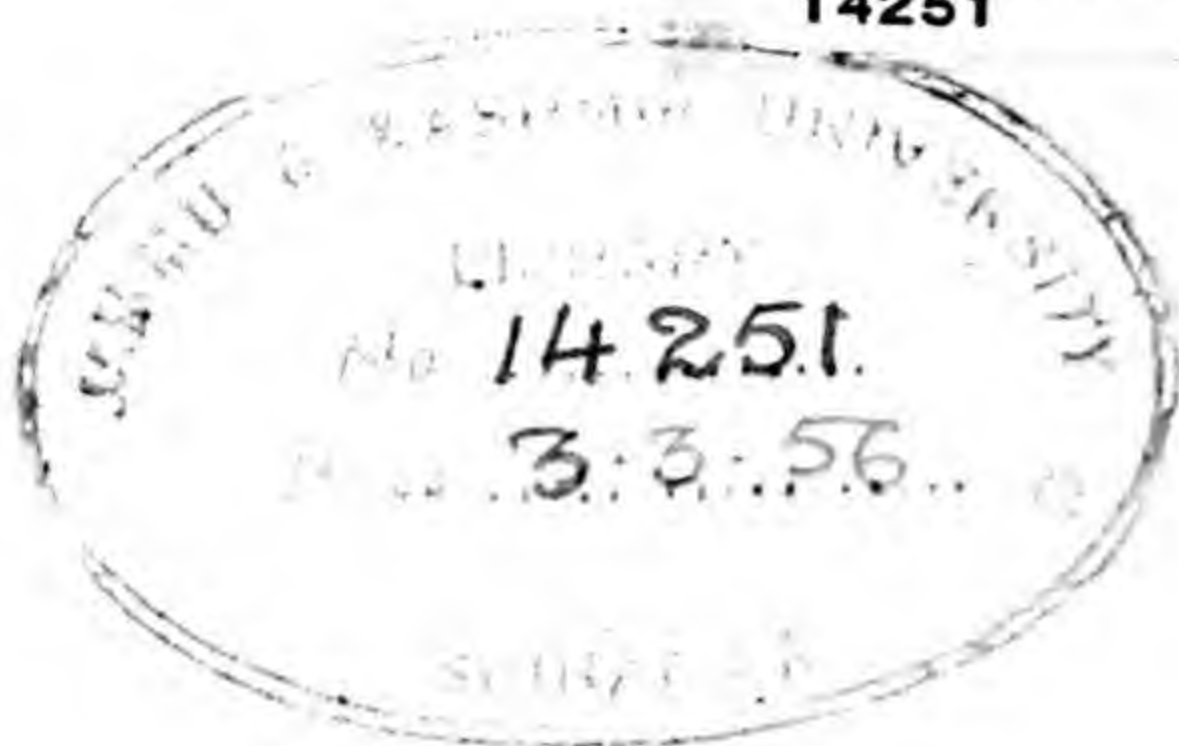
ZINC electro-plating, 388.
 — — refining, 393.



ALLAMA IQBAL LIBRARY



14251



PRINTED IN GREAT BRITAIN BY THE ABERDEEN UNIVERSITY PRESS, ABERDEEN

Title _____

Author _____

Accession No. _____

Call No. _____

**Borrower's
No.**

**Issue
Date**

**Borrower's
No.**

**Issue
Date**

Title _____

Author _____

Accession No. _____

Call No. _____

**Borrower's
No.**

**Issue
Date**

**Borrower's
No.**

**Issue
Date**

Title

Author

Accession No.

Call No.

**Borrower's
No.**

**Issue
Date**

**Borrower's
No.**

**Issue
Date**

Title _____

Author _____

Accession No. _____

Call No. _____

**Borrower's
No.**

**Issue
Date**

**Borrower's
No.**

**Issue
Date**

**The Jammu & Kashmir
University Library,
Srinagar.**

1. Overdue charge of one anna per-day will be charged for each volume kept after the due date.
2. Borrowers will be held responsible for any damage done to the book while in their possession.